

# SOME MICRO-CHEMICAL TESTS FOR ALKALOIDS

CHARLES H. STEPHENSON

SCIENTIFIC ASSISTANT

BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE,  
WASHINGTON, D. C.

INCLUDING

## CHEMICAL TESTS OF THE ALKALOIDS USED

C. E. PARKER

ASSISTANT CHEMIST

BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE,  
WASHINGTON, D. C.

With Twenty-seven Plates (162 Photomicrographs) and a  
Folding Table of Reactions.



LONDON

CHARLES GRIFFIN & COMPANY, LIMITED

12 EXETER STREET, STRAND, W.C. 2

1921

653  
547.7201543

N21

FIFTH EDITION, Thoroughly Revised. In Large 8vo. Cloth.  
With Tables and Illustrations. 36s. net.

## POISONS: Their Effects and Detention.

By A. WYNTER BLYTH, M.R.C.S., F.I.C., F.O.S.,

Barriester-at-Law, Public Analyst for the County of Devon, and  
Medical Officer of Health for St. Mary's Hospital.

AND M. WYNTER BLYTH, B.A., B.Sc., F.C.S.

GENERAL CONTENTS.—I.—Historical Introduction. II.—Classification. Statistics.—  
Connection between Toxic Action and Chemical Composition.—Life Tests. General  
Method of Procedure.—The Spectroscope.—Examination of Blood and Blood Stains.  
III.—Poisonous Gases. IV.—Acids and Alkalies. V.—More or less Volatile Poisonous  
Substances. VI.—Alkaloids and Poisonous Vegetable Principles. VII.—Poisons derived  
from Living or Dead Animal Substances. VIII.—The Oxalic Acid Group. IX.—  
Inorganic Poisons. Appendix: Treatment, by Antidotes or otherwise, of Cases of  
Poisoning.

"Undoubtedly THE MOST COMPLETE WORK on Toxicology in our language."—The Analyst.

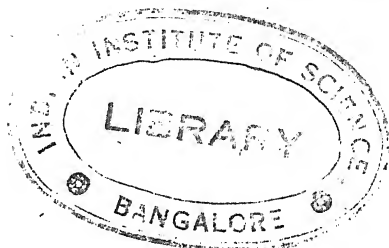
"AS A PRACTICAL GUIDE, WE KNOW NO BETTER WORK."—The Lancet.

LONDON: CHARLES GRIFFIN & CO., LTD., EXETER ST., STRAND, W.C.2.



Copyright, 1921, Charles H. Stephenson.

Printed by J. B. Lippincott Company, Philadelphia, U.S.A.



## CONTENTS

	PAGE
INTRODUCTION .....	1
MICROCHEMICAL TESTS FOR ALKALOIDS DESCRIBED BY OTHERS	3
CONCENTRATIONS OF ALKALOIDAL SOLUTIONS.....	7
REAGENTS USED.....	8
METHOD USED IN MAKING TESTS.....	11
SCHEME FOR IDENTIFICATION OF ALKALOIDS.....	13
TABLE SHOWING BEST TESTS FOR EACH ALKALOID.....	15
DETAILED DESCRIPTION OF TESTS.....	16
CHEMICAL EXAMINATIONS.....	84
INDEX TO PLATES.....	107
PLATES.....	111
TABLE OF REACTIONS.....	FOLLOWS PLATES

# SOME MICROCHEMICAL TESTS FOR ALKALOIDS

## INTRODUCTION

THIS work on microchemical tests for alkaloids was begun in December, 1907, in order to obtain microchemical tests for the detection of cocaine. From this beginning work was done on other alkaloids until a total of sixty-four had been tested. Thirteen of these alkaloids were of doubtful purity, and therefore the results obtained on these are not recorded here.

Two preliminary papers have been presented on this work before the Association of Official Agricultural Chemists, the first in 1908, published in Bulletin No. 122, Bureau of Chemistry, p. 97, 1909, and the second in 1910, published in Bulletin No. 137, Bureau of Chemistry, p. 189, 1911.

In this work no claim at all is made for originality in applying the microchemical tests for alkaloids, as the methods have been in use for many years. Most of the tests were worked out between the years 1907 and 1910, and since that time several of the more important contributions on the subject by other authors have been made. References to color reactions only have, in the main, been purposely omitted, since they were considered of minor importance for this work.

We have endeavored to give due credit for all microchemical tests which have been previously published and



## 2 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

which are described in this work, by referring in the text to tests already described by others.

While the results in some cases are not all that might be desired, yet some very sensitive and characteristic tests have been worked out. No tests whatever were obtained on three of the fifty-one alkaloids described. Tests on the other forty-eight alkaloids were, in most cases, quite satisfactory. Photomicrographs of all the more important crystalline precipitates obtained were made, and the most characteristic ones are given on plates.

Fungous growth takes place in many solutions of alkaloids after a time, an especially heavy growth occurring in brucine solutions. All of our work, however, was carried out on freshly prepared solutions.

The alkaloids with which the greatest number of crystalline precipitates were obtained, using the standard alkaloidal reagents, were strychnine, berberine, tropacocaine and brucine.

The alkaloids with which no crystalline precipitates were obtained were apocodeine, colchicine and solanine.

The following thirteen alkaloids were discarded because there was a serious doubt as to their purity: Bebeerine, cephaline, cornutine, delphinine, duboisine, emetine, gelseminine, lupinidine, pelletierine, sabadine, sabinine, sanguinarine and veratrine.

The author desires fully to acknowledge the assistance received from Mr. B. J. Howard, Microscopist in charge of the Microchemical Laboratory, not only for the many valuable suggestions made, but also for the taking of many of the photomicrographs herewith published.

## MICROCHEMICAL TESTS FOR ALKALOIDS DESCRIBED BY OTHERS

The following authors describe crystalline precipitates with alkaloids, which precipitates have also been investigated in this work:

1. T. G. Wormley, "Micro-chemistry of Poisons," 1869. Second edition 1885. This is the most exhaustive work in English which we have found on the subject. It gives microchemical tests for a great number of poisons other than alkaloids and deals with twelve alkaloids, describing crystalline precipitates for nine of them. It contains many fine plates showing the forms of the various crystalline precipitates. In the 1885 edition microchemical tests for gelsemine are given in addition to those described in the first edition.

2. J. W. Griffin and Arthur Henfrey, "The Micrographic Dictionary, a guide to the examination of the structure and nature of microscopic objects," 1883, vol. i, p. 30. Describes five crystalline precipitates which we have worked on.

3. A. W. Blyth, "Poisons: Their Effect and Detection," 1885. The following crystalline precipitates are described: Strychnine with potassium chromate; with potassium thiocyanate; with platinum chloride; with palladous chloride; and with gold chloride.

4. A. B. Lyons, "Notes on the Alkaloids of Coca Leaves," *The Am. Journ. Pharm.*, Oct., 1885, p. 30. Describes the crystalline precipitates with cocaine and the following reagents: Picric acid; gold chloride; platinum chloride; potassium hydroxide; and sodium carbonate. Gives

#### 4 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

sketches of the gold chloride and platinum chloride reactions.

5. F. Giesel, "Übermangansaures Kali zur Prüfung des Cocains," *Pharm. Zeit.*, Feb. 27, 1886. Describes the crystalline precipitate with cocaine and potassium permanganate.

6. Popoff, "Emploi de l'acide Picrique pour la détermination des alcaloïdes végétaux en toxicologie," *Annales d'Hygiène publique et de médecine légale*, 3e Serie 26, 1891, p. 81. The author describes crystalline precipitates with picric acid and gives sketches of the crystals produced. Eight of the crystalline precipitates described by him are formed in solutions of greater concentration than 1:50, and hence we do not describe them.

7. T. G. Wormley, "Notes on Some of the Chemical Properties of the Mydriatic Alkaloids," *Amer. Journ. Pharm.*, Nov., 1894, p. 513. Crystalline precipitates with the following reagents are described: Hyoscyne and gold chloride; atropine and hyoscyamine and also hyoscyne with picric acid. We did not obtain any crystalline precipitates with the two latter except in very concentrated solutions, and we have avoided, as a rule, describing the crystals formed in solutions more concentrated than 1:50.

8. H. Behrens, "Anleitung zur Mikrochemischen Analyse," vol. iii, 1st Edition, 1896. Three editions of this work have appeared. This is the most extensive work on microchemical analysis which has been published.

9. W. R. Dunstan and F. H. Carr, "Contributions to Our Knowledge of the Aconite Alkaloids," *The Pharm. Journ.*, Feb. 15, 1896, p. 122. The authors describe the crystalline precipitate with aconitine and potassium permanganate and that with cocaine and potassium permanganate.

10. M. Vadam, "Differentiation des alcaloides au moyen de leurs precipites microcristallins," *Journ. de Pharm. et de chimie*, 6 serie, 1897, ii, p. 100. Describes twenty-three different crystalline precipitates which we have studied.

11. B. Zenetti, "Den mikrochemischen Nachweis der Alkaloide mittelst Pikrinsäure (Festschrift zur Strassburger Versammlung des D. Ap.-V.)." Reference to above in *Pharm. Zeit.*, Nov. 3, 1897, vol. xlii, p. 752. Describes crystals formed with picric acid and the following alkaloids: Atropine, cocaine, nicotine, brucine, and strychnine.

12. W. H. Warren and R. S. Weiss, "The Picrolo-nates of Certain Alkaloids," *Journ. of Biol. Chem.*, 3, p. 327, 1907. Describes crystals formed with picric acid and alcoholic solutions of nicotine, strychnine and brucine.

13. Walter J. Dilling, "Coniine, Conhydrine, Pseudo-conhydrine, Coniceine, and a New Coniine Isomer. A Summary of Their Chemical Reactions," *The Pharm. Journ. and Pharmacist*, July 17, 1909, p. 102. Description of five crystalline precipitates with coniine, which we describe.

14. E. Abderhalden, "Handbuch des biochemischen Arbeitsmethoden," 1910, vol. ii, p. 904.

15. Alide Grutterink, "Beiträge zur mikrochemischen Analyse Einiger Alkaloide und Drogen mit besonderer Berücksichtigung der Methoden von H. Behrens," 1910. The author gives a table showing reactions of forty-two alkaloids and bases with sixty-nine reagents, and describes more fully reactions for sixteen alkaloids. In no other work which we have been able to locate have microchemical tests for so great a number of different alkaloids been

## 6 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

given, although there are only sixteen of the total forty-two alkaloids for which there are sketches and more complete descriptions of the precipitates.

16. L. Rosenthaler and P. Goerner, "Aromatic Nitro Derivatives, Especially Nitrophenols, as Alkaloidal Precipitants," *Z. Anal. Chem.*, 49, 1910, p. 340. Describes three crystalline precipitates with picric acid which we have described.

17. A. Bolland, "Mikrochemische Studien," *Monatshefte für Chemie* 29, 1908, p. 991; 32, 1911, p. 117. Describes many crystalline precipitates.

18. E. B. Putt, "Microchemical Tests for the Identification of Some of the Alkaloids," *J. Ind. Eng. Chem.*, vol. iv, p. 508-512, 1912. Describes seven crystalline precipitates that we have worked on. Fourteen photomicrographs are given.

## CONCENTRATIONS OF ALKALOIDAL SOLUTIONS

IN testing the alkaloids, aqueous solutions of from 1:1000 to 1:50 were used. In one case, however, a more concentrated solution than 1:50 was used, and that was with the alkaloid quinine, in which case a concentration of 1:35 was used. This more concentrated solution was used on account of the lack of satisfactory crystal formation in more dilute solutions. When the alkaloid or alkaloidal salt was not completely soluble in water, just sufficient 10 per cent. hydrochloric acid was added to dissolve it. In one or two cases only was an alcoholic solution of the alkaloid used, because the alkaloid was not soluble in water or in the 10 per cent. hydrochloric acid.

These solutions of alkaloids were tested with different reagents and the character of the precipitates, when formed, was noted under the microscope. After some time those reagents which were found to be unsatisfactory as alkaloidal precipitates were abandoned, and during the remainder of the work only those reagents which appeared of value were retained.

The final revised list of reagents which were found of value for tests numbers about forty.

## REAGENTS USED

The following reagents were used in 5 per cent. aqueous solutions: sodium carbonate; sodium nitroprusside; sodium phosphate; sodium benzoate; sodium phosphomolybdate; potassium hydroxide; potassium acetate; potassium iodide; potassium iodate; potassium chromate; potassium ferrocyanide and ferricyanide; potassium cyanide; potassium permanganate; saccharin; silver nitrate; ammonium molybdate; chromic acid; the chlorides of gold, platinum, palladium,\* mercury, iron and zinc; a 10 per cent. solution of barium nitrate; a saturated, aqueous solution of picric acid and the following reagents for which we give the formula:

Marme's reagent—Cadmium iodide .....	30 gms.
Potassium iodide .....	60 gms.
Distilled water .....	180 c.c.

Mayer's reagent—1:100 mercuric chloride in water and add just sufficient potassium iodide to redissolve the scarlet precipitate first produced.

Millon's reagent—dissolve metallic mercury in an equal weight of concentrated nitric acid and dilute with an equal volume of water.

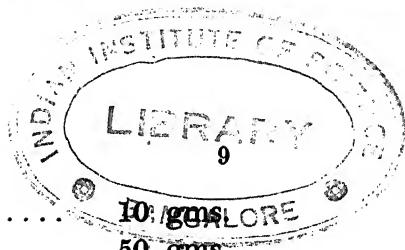
Zinc-chlor-iodide—Zinc chloride .....	100 gms.
Water .....	60 c.c.
Potassium iodide .....	20 gms.
Iodine crystals .....	6 gms.

---

\* Mr. E. B. Putt of this Bureau informs me that it is difficult to obtain a 5 per cent. aqueous solution of palladous chloride in a soluble form. What is ordinarily supplied as palladous chloride is either palladous-ammonium chloride or is a brown partially soluble powder that acts very much as if it contained considerable basic salt. If such a salt is encountered, it can be used only after being subjected to treatment with chlorine.

## REAGENTS USED

Wagner's reagent—Iodine .....	10 gms.
Potassium iodide .....	50 gms.
Water .....	1000 c.c.



Phosphomolybdic acid—sodium phosphomolybdate in 10 times its weight of a mixture of 1 part of strong nitric acid to 10 parts of water.

Phosphotungstic acid—dissolve 100 parts of sodium tungstate and 60 to 80 parts of sodium phosphate in 500 parts of water and add nitric acid until the reaction is acid.

Silicotungstic acid—a 5 per cent. aqueous solution.

Kraut's reagent—eighty grammes bismuth nitrate in 200 c.c. nitric acid of 1.18 sp. gr. Dissolve 272 grammes potassium iodide in a little water and add to above.

Ammonium thiocyanate—a 10 per cent. aqueous solution.

A saturated aqueous solution of sodium nitroprusside was used in addition to the 10 per cent. solution, but reactions with both solutions appear to be similar.

A 10 per cent. solution of picric acid in alcohol was used in addition to the saturated aqueous solution. The greatest difference noted was with atropine, in which case the alcoholic solution was much more sensitive in forming crystals than the aqueous solution.

The following reagents were used to test at least a part of the alkaloidal solutions, but they were not retained either because they reacted similarly to some reagent already on the list or because they did not form crystalline precipitates with the alkaloids under the conditions used in this work:

Ammonium hydroxide; barium carbonate; barium chloride; bismuth nitrate; bromine water; cadmium chlo-



## 10 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

ride; chloral hydrate; citric acid; ferric sulphate; phenol; phosphoric acid; potassium bromate; potassium bromide; potassium chloride; potassium fluoride; picrolonic acid; pyrogalllic acid; sodium bicarbonate; sodium citrate; sodium hydroxide; sodium hypochlorite; sodium nitrate; sodium salicylate; sodium sulphite; sodium tungstate; stannous chloride; strontium arsenate; strontium chromate; strontium nitrate; tannic acid; tartaric acid; uranium acetate; uranium nitrate; zinc sulphide.

## METHOD USED IN MAKING TESTS

To prepare the residue for testing it is usually essential that the alkaloid be separated from the product in as pure a form as possible by the usual chemical methods. Experiences with the tests have amply demonstrated the importance of this operation preliminary to applying the tests, and a considerable degree of purity is usually requisite to the successful operation of the test.

The alkaloid or alkaloidal residue to be tested is dissolved in water, and if not completely soluble sufficient 10 per cent. hydrochloric acid is added drop by drop until it is in solution. Care should be taken to keep all solutions to be tested as nearly neutral as possible, since the influence of free acid on the formation of crystalline alkaloidal compounds tends to break up or dissolve the crystals first formed.

Place one drop of the alkaloidal solution on a microscopic slide and add, by means of a glass rod, one small drop of the reagent. Examine for crystals under the microscope. Crystals are generally formed at once, though at times the slide must stand for a few minutes. In the latter case do not place cover glass on the solution, as crystallization is often due to concentration by evaporation.

By rubbing the slide with a glass rod crystallization is hastened, though the crystals are more likely to be abnormal when the solution is stirred. Precipitates which crystallize at all crystallize very quickly, as a rule, when stirred with a glass rod. In a few cases, however, crystals are not formed at all unless the solution be stirred. When stirred, the crystals are likely to be smaller and not so characteristic as when the crystals form more slowly. We recommend.

## 12 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

that stirring with a glass rod be avoided as far as possible on account of the abnormal crystal forms likely to be thus obtained. However, stirring serves a useful purpose in many cases and is often a desirable procedure.

Care should be taken that the glass rod used in making the test is properly cleaned between each test, otherwise it serves to carry at least a trace of crystalline matter from one test over into the next.

It is desirable to make up the alkaloid to be tested to known strength, as the crystals formed show such variation in many cases dependent upon concentration.

The amount of reagent used has usually great effect upon the formation of crystals. Sometimes a very small amount of reagent gives the best crystals, then again a considerable amount is needed in order to get crystal formation at all. Normally an amorphous precipitate is formed which soon crystallizes, though at times the crystals are formed directly without the amorphous precipitate being first thrown down.

With some alkaloids, notably berberine and narcotine, similar crystals are formed with a great number of different reagents, and it appears that the alkaloid is thrown out of the solution by the addition of the reagent rather than that a salt is formed.

**LIMIT OF REACTION.**—In every case where we get crystal formation in the 1:1000 solution of the alkaloid, a more dilute solution was used in order to report the approximate greatest dilution with which crystals are formed. It will be noted that in some reactions, cocaine with gold-chloride, for example, crystals are produced at dilutions of as great as 1:20,000. Such a reaction is a very sensitive one and with it we can identify mere traces of alkaloid.

## SCHEME FOR IDENTIFICATION OF ALKALOIDS

The following outline may be of service in identifying the alkaloids, though it has thus far been found impossible to make out what is considered a satisfactory key for use in their identification.

If any alkaloid is suspected, find it on the list and use the reagent under which it is placed. For example, in testing for atropine, use Wagner's reagent for cocaine, gold chloride, etc.

The alkaloids in the following lists are not the only ones which form crystals with the reagents in question, but each alkaloid is listed under that reagent with which it forms the most satisfactory crystals for identification.

Characteristic crystalline precipitates are formed with each reagent and alkaloids in the list following it.

### WITH GOLD CHLORIDE SOLUTION

1. Cocaine
2. Tropacocaine
3. Benzoyl-ecgonine
4. Strychnine
5. Caffeine
6. Quinidine
7. Quinoline
8. Apomorphine
9. Nicotine
10. Sparteine
11. Scopolamine

### WITH KRAUT'S REAGENT

1. Theobromine
2. Narceine
3. Anhalonine
4. Coniine
5. Arecoline

### WITH POTASSIUM HYDROXIDE SOLUTION

1. Thebaine
2. Papaverine
3. Narcotine
4. Hydrastine
5. Aspidospermine
6. Corydaline
7. Chelidonium

### WITH WAGNER'S REAGENT

1. Homatropine
2. Hyoscyamine
3. Berberine
4. Atropine
5. Colchicine

### WITH PLATINUM CHLORIDE SOLUTION

1. Calycanthine
2. Pilocarpine
3. Brucine
4. Cinchonidine

## 14. SOME MICROCHEMICAL TESTS FOR ALKALOIDS

### WITH PHOSPHOTUNGSTIC ACID

1. Betaine
2. Pilocarpidine
3. Pelleterine

### WITH PHOSPHOMOLYBDATE

1. Choline
2. Ecgonine

### WITH MARME'S REAGENT

1. Morphine
2. Codeine

### WITH SODIUM CARBONATE

1. Cinchonine
2. Aconitine

### WITH MERCURIC CHLORIDE

1. Heroin
2. Dionine

### WITH POTASSIUM PERMANGANATE

Hydrastinine

### WITH MAYER'S REAGENT

Cytisine

### WITH SODIUM PHOSPHATE

Quinine

### WITH POTASSIUM IODIDE

Petonine

### WITH POTASSIUM CYANIDE

Yohimbine

# TABLE SHOWING BEST TESTS FOR EACH ALKALOID

(Roman numerals refer to Plates, Arabic to Figures)

	<i>Best</i>	<i>Second</i>
1. Aconitine	Sodium Carbonate (XIII, 6)	Potassium Permanganate
2. Anhalomine	Kraut's Reagent	Platinum Chloride (IV, 1)
3. Apocodrine	No tests	
4. Apomorphine	Gold Chloride (I, 2)	Chromic Acid
5. Arecoline	Kraut's Reagent	Palladium Chloride (VI, 1)
6. Aspidospermine	Potassium Hydroxide (XV, 1)	Wagner's Reagent (X, 1)
7. Atropine	Wagner's Reagent (X, 2)	Picric Acid (XIX, 1)
8. Benzoyl-ecgonine	Gold Chloride (I, 3)	Wagner's Reagent
9. Berberine	Chromic Acid	Hydrochloric Acid (XX, 5)
10. Retaine	Phosphotungstic Acid (XXIV, 4)	Kraut's Reagent
11. Brucine	Platinum Chloride (IV, 2)	Palladium Chloride (VI, 2)
12. Caffeine	Kraut's Reagent (XIII, 2)	Gold Chloride (I, 4)
13. Calycanthine	Platinum Chloride (IV, 3)	Palladium Chloride (VI, 6)
14. Chelidamine	Potassium Hydroxide	Potassium Ferrocyanide
15. Choline	Phosphomolybdic Acid (XXIV, 2)	Silicotungstic Acid
16. Cinchonine	Sodium Carbonate (XIV, 1 and 2)	Potassium Ferrocyanide
17. Cinchonidine	Platinum Chloride (IV, 4)	Potassium Hydroxide
18. Cocaine	Gold Chloride (I, 5 and 6)	Platinum Chloride (IV, 5)
19. Codeine	Marme's Reagent (XVII, 1, 2 and 3)	Wagner's Reagent (X, 6)
20. Colchicine	No tests	
21. Conine	Phosphotungstic Acid (XXIV, 5)	Marme's Reagent (XVII, 4)
22. Corydalline	Potassium Hydroxide	Mercuric Chloride (VIII, 2)
23. Cytisine	Mayer's Reagent	Wagner's Reagent (XI, 1)
24. Dioneine	Wagner's Reagent (XI, 2)	Mercuric Chloride (VIII, 4)
25. Equisetine	Phosphomolybdic Acid	Phosphotungstic Acid
26. Herosine	Mercuric Chloride (VIII, 5)	Sodium Carbonate
27. Homatropine	Wagner's Reagent (XI, 3 and 4)	Gold Chloride (II, 2)
28. Hydrastine	Potassium Hydroxide (XV, 4)	Chromic Acid (XXII, 5)
29. Hydrastinine	Potassium Permanganate (XXIII, 5)	Kraut's Reagent
30. Hyoscyamine	Wagner's Reagent (XI, 5)	Wagner's Reagent (XI, 6)
31. Morphine	Marme's Reagent (XVII, 5)	Platinum Chloride (V, 1)
32. Narceine	Wagner's Reagent (XII, 1)	Potassium Acetate (XII, 5)
33. Narceotine	Potassium Hydroxide	Mercuric Chloride (IX, 1)
34. Nicotine	Gold Chloride (II, 5)	Zinc Chloride (XXVI, 6)
35. Papaverine	Potassium Hydroxide (XV, 5)	Ammonium Thiocyanate
36. Peruvine	Potassium Iodide (XVIII, 2)	
37. Physostigmine	Gold Chloride	
38. Phloxaridine	Phosphotungstic Acid (XXIV, 6)	Phosphomolybdic Acid
39. Phloxaridine	Platinum Chloride (V, 2)	Gold Chloride
40. Piperine	Mercuric Chloride	Platinum Chloride
41. Quinine	Sodium Phosphate (VII, 6)	Wagner's Reagent (XII, 2)
42. Quinidine	Gold Chloride (II, 6)	Ammonium Thiocyanate (XXV, 5)
43. Quinoline	Gold Chloride (III, 1)	Kraut's Reagent (XIII, 4)
44. Scopolamine	Gold Chloride (III, 2)	Wagner's Reagent (XII, 4)
45. Solanine	No tests	
46. Sparteine	Gold Chloride (III, 3)	Palladium Chloride (VII, 2)
47. Strychnine	Gold Chloride (III, 4)	Chromic Acid (XXIII, 2)
48. Thebaine	Potassium Hydroxide (XVI, 2)	Platinum Chloride
49. Theobromine	Picric Acid	Kraut's Reagent
50. Tropacocaine	Gold Chloride	Platinum Chloride (V, 5)
51. Yohimbine	Potassium Cyanide (XXI, 3)	

## DETAILED DESCRIPTION OF TESTS

It will be noted that the alkaloids are treated in alphabetical order. The descriptions are kept short, and many of the crystal forms produced can, at least, be but poorly described.

Reference is made in the text to all crystal forms reproduced in the plates. Many of the precipitates photograph very poorly, and for this reason some sensitive tests have not been reproduced in the plates.

### ACONITINE.

Four crystalline and twenty-two non-crystalline precipitates were obtained.

**SODIUM CARBONATE.**—This is the most sensitive test for aconitine. Characteristic rosettes are usually slowly formed in great numbers even in the 1:1000 solution. They are usually formed more quickly in the 1:500 solution than in the 1:200 solution. Amorphous precipitates form in the two more concentrated solutions only (Plate XIII, Fig. 6).

**POTASSIUM PERMANGANATE.**—The precipitates are rather dense. The crystals are small, spherical, and form very slowly in the two more dilute solutions. In the 1:200 solution the crystals are rosettes and polarize brightly. They are characteristic and of good size. Not many are formed and they form slowly (9).

**POTASSIUM HYDROXIDE.**—In the 1:200 solution the amorphous precipitate crystallizes in rosettes of short-pointed rods. Crystals are often formed in few numbers only and very slowly.

Potassium cyanide gives results similar to the above.

Ammonium thiocyanate gives a very slight precipitate in the 1: 50 solution only.

#### ANHALONINE (MESCALINE)

The microchemical reactions of two samples, one labeled "Mescaline" and the other "Anhalonine," were identical. Attention is called to the melting point obtained by Parker,  $181-2^{\circ}$  as compared with Schmidt's figure recorded as  $254-5^{\circ}$ .

Four aqueous solutions of the alkaloid were used, *viz.*: 1: 1000; 1: 500; 1: 200; 1: 50.

Non-crystalline precipitates formed only with zinc-chloride, phosphomolybdate, and silico-tungstic acid.

With this alkaloid eleven crystalline precipitates were obtained as follows:

**KRAUT'S REAGENT.**—This is the most sensitive test, great numbers of very small crystals being formed even in a 1: 3000 solution. They are too small, however, to be of service as a test. The best concentration for crystal formation is about 1: 200. At this concentration they are often very large and moss-like in appearance and polarize only slightly. An amorphous precipitate is thrown down first from which the crystals form quickly.

**GOLD CHLORIDE.**—This reagent does not form crystals in the 1: 1000 solution, but small crystals, quickly growing to a good size, are formed upon stirring the 1: 500 solution.

Very large rods, in a dense mass, form in the 1: 50 solution, and of good size in the 1: 200 solution (Plate I, Fig. 1) (17).

**PLATINUM CHLORIDE.**—This reagent forms a few small crystals on stirring the 1: 500 solution. A dense



## 18 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

mass of large, fine needle rosettes was instantly formed in the 1: 50 and 1: 200 solutions (Plate IV, Fig. 1) (17).

**PICRIC ACID.**—An amorphous precipitate formed in the 1: 50 solution only, and this crystallizes very rapidly into large, rough-appearing rods. Large rods are also formed in the 1: 200 solution, but without a first amorphous precipitate. Upon stirring the two more dilute solutions we get a great number of small rods (17).

**WAGNER'S REAGENT.**—This reagent forms heavy amorphous precipitates in the two more concentrated solutions which crystallize slowly into large, rough-appearing rods of a bluish-black to black color. Their polarization is slight. The slight amorphous precipitate in the 1: 500 solution does not crystallize, but upon stirring with a glass rod great numbers of small rods are formed even in the 1: 1000 solution if sufficient reagent be added (17).

**MERCURIC CHLORIDE.**—Upon stirring the 1: 50 solution great numbers of large, highly polarizing rosettes either of plates or of rods are formed (17).

**POTASSIUM PERMANGANATE.**—This reagent forms very short rods in the 1: 50 solution only on stirring.

**PALLADOUS CHLORIDE.**—Clear-cut, highly polarizing crystals are formed in the 1: 50 solution on stirring and a very few in the 1: 200 solution. They are normally four- or six-sided.

**MAYER'S REAGENT.**—This reagent forms amorphous precipitates in the two more concentrated solutions only. Crystals form quickly and are rosettes of rods or plates.

**MARME'S REAGENT.**—Large plates or rosettes of rods formed in the 1: 50 solution.

**PHOSPHOTUNGSTIC ACID.**—This reagent forms crystals slowly in all solutions from the amorphous precipitate.

They are rosettes of short rods and in the 1:50 solution often very large rods (Plate XXIV, Fig. 3). Froehde's reagent gives a yellow color.

#### APOCODEINE

No crystalline precipitates were obtained whatever with this alkaloid.

All of the common alkaloidal reagents form heavy non-crystalline precipitates.

#### APOMORPHINE

The solutions of this alkaloid take on a light, greenish color within a few minutes and turn to a dark blue after a few hours.

Ten crystalline and twenty-five non-crystalline precipitates were obtained.

**GOLD CHLORIDE.**—This is the best test for apomorphine.

Heavy amorphous precipitates appear in all the solutions at once and they are of a deep, red-brown color. The crystals are formed in dense masses and do not polarize. They are small and very fine needles in all the solutions, being somewhat larger in the more concentrated solutions and are occasionally rosettes.

This test is very sensitive, as we are able to obtain fine needles in a 1:10,000 solution (Plate I, Fig. 2).

**PLATINUM CHLORIDE.**—Crystals formed from amorphous precipitate in all solutions except the 1:50. They are characteristic, rather small rosettes, of a deep rose color.

**CHROMIC ACID.**—Very faint rose color in the 1:1000 solution and precipitates in the 1:500 and more concentrated solutions which are reddish-brown turning to green around the edges.

## 20 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Crystals are small and formed in all solutions. They do not polarize. Normally rosettes of short rods. The crystals in the 1:50 are considerably larger.

POTASSIUM IODIDE.—Amorphous precipitate in the 1:50 solution only, and this crystallizes into small, highly polarizing crystals which have sharp, clear-cut angles like those of a diamond. The 1:200 solution does not form a precipitate.

Potassium iodide gives reactions similar to above.

ZINC CHLORIDE.—Small rods in rosettes instantly formed in the 1:50 solution only.

KRAUT'S REAGENT.—Large rosettes of rods are formed at once in the 1:50 solution in addition to the heavy brown precipitate which does not crystallize.

PHOSPHOMOLYBDIC ACID.—A dense mass of rod-like crystals instantly formed in the 1:50 solution only.

MILLON'S REAGENT.—Rose-red precipitate forming rods in the 1:50 solution and these are often in rosettes. No crystals formed in the more dilute solutions.

Barium nitrate and silver nitrate give crystals similar to those formed with this reagent and in the 1:50 solution only.

The following color reactions were noted:

Rose-red color with ferric sulphate and also with silver nitrate and ammonium vanadate. Red precipitate turning to deep green with potassium chromate and ferric chloride.

### ARECOLINE HYDROBROMIDE

Four crystalline and ten non-crystalline precipitates were obtained. Only one satisfactory test was worked out for this alkaloid.

KRAUT'S REAGENT.—Crystals are formed slowly from

the amorphous precipitates in the two more concentrated solutions, but are formed more quickly in the two dilute solutions. They are good-sized plates often in rosettes. The test is sensitive, as great numbers of crystals are formed in the 1:1000 solution (Plate XIII, Fig. 1).

**PICRIC ACID.**—Not a sensitive test and no amorphous precipitates are formed. As the 1:50 solution evaporates, spherical crystals or rosettes of short rods of good size are formed.

**PALLADOUS CHLORIDE.**—After the 1:50 solution stands for some time large irregular plates which polarize well are formed. These plates are often in rosettes (Plate VI, Fig. 1).

**MILLON'S SOLUTION.**—In the 1:50 solution only, small needle-shaped crystals, often in rosettes, are formed from the amorphous precipitate.

#### ASPIDOSPERMINE

Eight crystalline and twenty-four non-crystalline precipitates were obtained.

**POTASSIUM HYDROXIDE.**—A fine and sensitive test. Fine large crystals are quickly formed from the amorphous precipitate. They are about the same in appearance in all solutions, though much larger in the more concentrated solutions. They form a dense mass of rosettes in the 1:50 solution. Their appearance is similar to that of some forms of seaweed (Plate XV, Fig. 1).

Small rods formed in a 1:3000 solution, which is about the limit of reaction. Potassium chromate, sodium carbonate, and potassium cyanide give crystals similar to above, though they are not so sensitive.

**WAGNER'S REAGENT.**—Very short, pointed rods in

## 22 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

rosettes are formed in the two more concentrated solutions only. They are formed around the edges of the heavy amorphous precipitates (Plate X, Fig. 1).

Potassium iodide, Mayer's reagent, and Marme's reagent all give results similar to the above.

The following color reactions were noted:

With ferric chloride a deep rose color is developed in addition to the amorphous precipitate.

With potassium iodate a faint pink color develops in the 1:50 solution on standing.

The amorphous precipitate with gold chloride takes on a black color.

With chromic acid the amorphous precipitate takes on a pink color.

### ATROPINE SULPHATE

Four crystalline and thirteen non-crystalline precipitates were obtained.

**WAGNER'S REAGENT.**—This is a sensitive test and the best one that we have for atropine. The crystals are normally small rods or triangular plates and are formed in great numbers from the amorphous precipitate first thrown down. They have sharp angles and polarize poorly. A 1:8000 solution forms great numbers of very small crystals. The crystals in the 1:50 solution are of good size. This is a satisfactory test, and though the crystals are never large, they are characteristic (Plate X, Figs. 2 and 3) (18).

Zinc-chlor-iodide or Kraut's reagent forms crystals similar to the above.

**PICRIC ACID.**—We have an amorphous precipitate but no crystals in solutions above 1:50. Crystals are obtained with difficulty and only in the 1:50 solution. They are

normally large, plate-like and polarize brilliantly. Crystal formation is so uncertain as to make this reaction of no value as a test. This test is described by Wormley, he, however, using an alcoholic solution of picric acid rather than an aqueous solution (1). The alcoholic solution of picric acid makes a very satisfactory reagent for this alkaloid, as upon stirring the 1:1000 solution small plates are formed and from the amorphous precipitates in the other solutions rosettes of plates are formed (Plate XIX, Fig. 1) (6) (10) (11).

Potassium hydroxide forms an amorphous precipitate in the 1:50 solution but not in the 1:200 solution.

Wormley describes a crystalline precipitate with potassium hydroxide, but we have been unable to confirm this (1).

#### BENZOYL-ECGONINE

Five crystalline and nine non-crystalline precipitates were obtained.

**GOLD CHLORIDE.**—Amorphous precipitates are formed in all solutions. This is the only sensitive test. Crystals form from the amorphous precipitates rather quickly. They grow to large size, are light greenish-yellow in color and polarize brightly. They are normally rosettes of long and rather narrow irregular plates. They form a dense mass in the 1:50 solution. The photograph reproduced was taken just after the crystallization had started. Crystals of good size are formed in a 1:3000 solution after it stands for some time (Plate I, Fig. 3).

**WAGNER'S REAGENT.**—Heavy, amorphous precipitates in all solutions, but crystals are formed only in the two more concentrated solutions. These crystals are large and dense rosettes appearing like some form of seaweed. Only

## 24 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

a few crystals are formed in the 1:200 solution. These crystals are of a light greenish color and polarize fairly well.

Kraut's reagent reacts as above.

**MAYER'S REAGENT.**—Very long, needle-like crystals are formed in the two more concentrated solutions only and around the edges of the drops.

Palladous chloride forms an amorphous precipitate in the 1:50 solution only.

The amorphous precipitate with potassium permanganate and with mercuric chloride is very slight.

### BERBERINE

A saturated aqueous solution, this being about 1:100, also solutions of 1:500 and 1:1000 were used. The solutions of this alkaloid are yellow.

Upon addition of the following reagents to a saturated aqueous solution in addition to a heavy amorphous precipitate, crystals are formed. The crystals show up to better advantage if but little of the reagent be used.

The crystals are similar, if not identical, with all of the reagents in the following list: Chromic acid; sodium nitroprusside; platinum chloride; palladous chloride; mercuric chloride; zinc-chlor-iodide; Wagner's reagent; potassium iodide; Kraut's reagent; Marme's reagent; phosphomolybdic acid; saccharin; ammonium thiocyanate; potassium permanganate (2); picric acid; sulphuric acid; hydrochloric acid; ferric chloride; zinc chloride; Millon's reagent; barium and silver nitrate. They are in all cases moss-like or fine needles, often in rosettes, and the greater part of the heavy amorphous precipitate does not crystallize (Plate X, Fig. 4, and Plate XX, Figs. 5 and 6) (8).

The reagents with which no crystals were obtained are: Potassium cyanide; ammonium molybdate; gold chloride; Mayer's reagent; potassium ferrocyanide; potassium ferricyanide; silico-tungstic acid and phosphotungstic acid.

Berberine, upon evaporation of the aqueous solution, crystallizes into yellow needles, often in rosettes.

### BETAINES HYDROCHLORIDE

Eight crystalline and three non-crystalline precipitates were obtained.

**PHOSPHOTUNGSTIC ACID.**—This is a fine, sensitive and characteristic test. Crystals are formed at once in all solutions, and they form a very dense mass in the two more concentrated solutions. The crystals are of two kinds, long needles in rosettes and very short rods in rosettes. The limit of reaction is about 1:2000 (Plate XXIV, Fig. 4).

**KRAUT'S REAGENT.**—A few needles are formed in the 1:1000 solution. Amorphous precipitates in the three more concentrated solutions only and crystals are slowly formed from this unless the solutions are stirred, but if stirred, the crystals are formed quickly, being needles usually in rosettes, though often six-sided crystals are formed.

**PHOSPHOMOLYBDIC ACID.**—There is no precipitate in the 1:1000 solution.

Great numbers of small spherical crystals are formed and also needles and often rods in the 1:500 solution. Reactions are best at this dilution. Large rosettes of needles or rods are formed slowly in the two more concentrated solutions, the needles with pointed ends and rods irregular in outline. The amorphous precipitates are heavy in the more concentrated solution (Plate XXIV, Fig. 1).



## 26 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

**PICRIC ACID.**—Crystals of rods and needles are formed on stirring the 1: 50 solution only. This is not at all sensitive as a test.

With the alcoholic solution of picric acid they are formed in the two more concentrated solutions.

**WAGNER'S REAGENT.**—Only in the 1: 50 solution are crystals formed on stirring. They are characteristic plates in rosettes.

**GOLD CHLORIDE.**—Crystals are formed only on stirring the 1: 50 solution. They are usually regular rods and sometimes there are a few plate-like forms. They polarize well.

**SILICO-TUNGSTIC ACID.**—The amorphous precipitates formed in the two more concentrated solutions only crystallize. Crystals are very small and polarize but slightly. They are normally short rods.

**SODIUM BENZOATE.**—Crystals are formed in the 1: 50 solution only and they are rosettes of plates and are exactly like those formed when hydrochloric acid is added to a sodium benzoate solution.

The following color reaction was noted:

Ammonium vanadate when added to a little of the alkaloid gives a red color which fades quickly.

### BRUCINE

Twenty crystalline and nine non-crystalline precipitates were obtained.

**POTASSIUM HYDROXIDE.**—Tufts of needle-shaped crystals are formed in the 1: 200 solution. This is the greatest dilution that forms crystals at once and then only on stirring. Very large rosettes of needles are quickly formed from the heavy amorphous precipitate in the 1: 50 solu-

tion. These crystals grow to large size and may easily be seen without the aid of the microscope.

In the more dilute solutions tufts of needle crystals are formed from the amorphous precipitate only after some time and as the solutions evaporate (Plate XV, Fig. 2) (1) (8).

Sodium carbonate gives results similar to the above (8).

**SODIUM NITRO-PRUSSIDE.**—Spherical crystals are formed in the 1: 200 solution on standing. They are small and show distinct polarization crosses. Rosettes formed from the amorphous precipitate in the 1: 50 solution. No precipitate is formed in the more dilute solutions (Plate IX, Fig. 6).

**CHROMIC ACID.**—Great numbers of rods, often in rosettes, are formed in a 1: 1000 solution. The crystals are large and in a dense mass in the more concentrated solutions. A great number of small crystals were formed in a 1: 4000 solution (Plate XXII, Fig. 1).

Chrom-acetic acid gives crystals similar to above, but they are formed without an amorphous precipitate being first thrown down.

**POTASSIUM CHROMATE.**—In the three more concentrated solutions rods often in rosettes are formed. Often the rods have a twisted or spiral appearance (8) (10).

**PLATINUM CHLORIDE.**—This is a very sensitive test. The 1: 1000 solution crystallizes out into a dense mass of rods which are sometimes in rosettes. The crystals in the 1: 50 solution are small, as it is too concentrated for best results. A considerable number of small crystals are formed in a 1: 20,000 solution (Plate IV, Fig. 2) (1) (8) (10).

**PALLADOUS CHLORIDE.**—Rods formed in all solutions

up to 1:4000. At the latter dilution we get very few small crystals. These rods are normally in rosettes and formed from an amorphous precipitate. In the 1:500 solution an amorphous precipitate is first formed and the crystals are not large and polarize poorly. The 1:50 solution is too concentrated for best results and the crystals vary greatly in size (Plate VI, Fig. 2).

**MERCURIC CHLORIDE.**—A light precipitate is obtained in the 1:500 and 1:1000 solution from which spherical or rosette crystals are formed. The crystals are fine rosettes of plates in the more concentrated solutions. The addition of too great an amount of reagent hinders the formation of crystals greatly (8).

**ZINC CHLORIDE.**—The crystals are clear-cut rods or plates with sharp angles in rosettes, and the limit of reaction is about 1:500 (Plate XXVI, Fig. 5).

**ZINC-CHLOR-IODIDE.**—Limit of reaction is about 1:200. Crystals are spherical or rosettes and like those obtained in the zinc chloride reaction.

**AMMONIUM THIOCYANATE.**—The slight amorphous precipitate in the 1:50 solution crystallizes quickly into moss-like rosettes (Plate XXV, Fig. 1) (2).

**WAGNER'S REAGENT.**—Heavy precipitates form in all the solutions. Crystallization is slow and the crystals are small rosettes except in more concentrated solutions, when they are large rosettes or rods. The limit of reaction is about 1:2000 (Plate X, Fig. 5).

**POTASSIUM IODIDE.**—No amorphous precipitates are obtained with this reagent. Large, brightly polarizing masses of plates, often in rosettes, are formed in the two more concentrated solutions in great numbers. Crystals are formed very slowly in the 1:500 solution. These crys-

DETAILED DESCRIPTION OF TESTS

tals have a characteristic appearance (Plate XVIII, Fig. 2).

**KRAUT'S REAGENT.**—A dense precipitate but no crystals are formed in the 1:1000 solution. A few good-sized rosettes are formed in the 1:500 solution. They appear to float at the surface. In the more concentrated solutions we have another form of crystals also present. They are smaller and darker and rosettes are formed slowly.

**MARME'S REAGENT.**—Very dense, amorphous precipitates are obtained only in the three more dilute solutions. Crystals form only in the 1:50 solution. They are the same as those formed with potassium iodide; that is, rosettes composed of rods.

**POTASSIUM FERRICYANIDE.**—Crystals quickly form in the 1:50 solution only from the dense, amorphous precipitate. They are large rosettes of plates and polarize brightly. Many of the crystals are needles and sometimes a combination of needles and plates is obtained. They are very brilliant under polarized light (1).

**POTASSIUM CYANIDE.**—Crystals form in the two more concentrated solutions only and in general outline look like some form of grass in the 1:200 solution, and large rosettes in the 1:50 solution. A dense, amorphous precipitate is first formed in the 1:50 solution (Plate XXI, Fig. 1).

**SACCHARIN.**—Great numbers of small needles are formed on stirring the 1:200 solution and are slowly formed in the 1:50 solution, in which case we have rosettes of needles, or often of plates. No crystals or precipitates are obtained in the two more dilute solutions (Plate V, Fig. 6).

**PICRIC ACID.**—This is a poor test, as crystals form slowly and often not at all, and then in concentrated solu-

686  
547.7201543  
A21

### 30 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

tions only. They are rosettes of needles (1) (6) (10) (11) (12).

**MILLON'S REAGENT.**—A slight precipitate is formed in the 1:200 solution and it redissolves. There is a faint rose-red color which forms rather slowly and starts around the edge of the drop. On standing, brilliant crystals are formed. The crystals are rosettes of small plates and polarize well (Plate XXVI, Fig. 1).

Upon addition of water to some brucine crystals, they change from irregular plates to fine rosettes of needles and these in turn dissolve as more water is added.

The brucine solutions upon standing several weeks become a faint pink color.

The following color reaction was noted: Add one drop of chromic acid and then one drop of concentrated hydrochloric acid. A deep blood-red is then developed. Crystals are formed similar to those formed with a chromic acid alone.

#### CAFFEINE

Six crystalline and two non-crystalline precipitates were obtained.

**KRAUT'S REAGENT**—This is the best test for caffeine.

In the 1:1000 solution a heavy, amorphous precipitate is formed which crystallizes quickly in dark, reddish-brown rosettes of small size. The 1:500 and 1:200 solutions give similar results. These crystals do not polarize.

The precipitate is so dense in the 1:50 solution that it hinders crystallization somewhat. Many of the crystals are small rods. A 1:5000 solution forms some very small crystals (Plate XIII, Fig. 2).

**MERCURIC CHLORIDE.**—A considerable number of

needle-shaped crystals are formed in all solutions. They form a dense mass in the 1:50 solution and polarize brilliantly. The limit of reaction is about 1:1000 (Plate VIII, Fig. 1).

**PALLADOUS CHLORIDE.**—The limit of reaction is about 1:200. The crystals are small needles and form a dense mass in the 1:50 solution. They polarize but slightly.

**GOLD CHLORIDE.**—This is not a sensitive test. The crystals are normally needles or tufts of needles and form very slowly. In the 1:50 solution tufts or rosettes of fairly large rods or needles are formed on standing (Plate I, Fig. 4) (10).

**PHOSPHOMOLYBDIC ACID.**—Heavy, amorphous precipitates form. Crystals are small rods usually formed around the edges. In the 1:200 solution the crystals are small and in great numbers. They do not stand out clearly on account of being massed and often surrounded by the amorphous precipitate. In the 1:50 solution the precipitate is so dense that the crystals form slowly. They are normally rods.

**SILICO-TUNGSTIC ACID.**—In the two more concentrated solutions the crystals are very small and the amorphous precipitates are dense. The crystals do not polarize brightly.

#### CALYCANTHINE SULPHATE

Thirteen crystalline and fifteen non-crystalline precipitates were obtained.

**PLATINUM CHLORIDE.**—This is a sensitive test. An amorphous precipitate is formed which crystallizes almost instantly into cross-like crystals in all solutions. They appear especially well in the 1:50 solution (Plate IV, Fig. 3).

### 32 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

**CHROMIC ACID.**—Amorphous precipitates appear in the three more concentrated solutions only. These precipitates crystallize on standing, forming fine, large rosettes of needles or rods, especially large in the 1: 50 solution (Plate XXII, Fig. 2).

**PALLADOUS CHLORIDE.**—This is a sensitive test. Crystals are quickly formed in all the solutions. They are very large and even in the 1: 1000 solution they are of good size. Great numbers of small rods are formed on stirring the 1: 2000 solution (Plate VI, Fig. 3).

**ZINC-CHLOR-IODIDE.**—Amorphous precipitates appear in all the solutions. Very small crystals were noticed only in the 1: 500 solution after it had stood for some time, but most of the precipitate does not crystallize.

**WAGNER'S REAGENT.**—Amorphous precipitates formed in all the solutions and crystals in all but the 1: 1000 solution. Crystals are irregular plates often occurring in rosettes. They are very small in the 1: 500 solution, but form quickly and are of large size in the 1: 50 solution.

**AMMONIUM THIOCYANATE.**—A dense mass of rods is formed in the 1: 50 solution. Stir the 1: 500 solution for quick crystallization.

**POTASSIUM CYANIDE.**—The crystals are small and triangular in outline. They are quickly formed in the two more dilute solutions on stirring. They are large and form quickly from the precipitate in the 1: 50 solution.

Potassium hydroxide or sodium carbonate gives results similar to those above.

**KRAUT'S REAGENT.**—Very large, deep, yellow, irregular plates are formed in the two more concentrated solutions only from the dense, amorphous precipitates.

**POTASSIUM IODIDE.**—Large rosettes of rods are formed

instantly upon stirring the 1: 50 solution and in the 1: 200 solution on standing.

**SODIUM PHOSPHATE.**—Crystals are only formed in the 1: 50 solution. They form slowly. They are rather small, clear-cut rosettes growing to good size.

The following color reaction was noted:

Ammonium vanadate gives a blood-red color, which quickly fades, in the 1: 50 solution.

**SODIUM NITROPRUSSIDE.**—A concentrated aqueous solution of the reagent was used.

The dense, amorphous precipitate quickly crystallizes in the 1: 50 solution only in fine large rosettes of plates. On stirring the 1: 500 solution small six-sided plates are formed.

#### CHELIDONINE

Twelve crystalline and twenty non-crystalline precipitates were obtained.

**POTASSIUM HYDROXIDE.**—This is the best test for chelidonine.

The amorphous precipitate crystallizes quickly in all solutions. The crystals in the 1: 1000 solution are good-sized, irregular rods and polarize well. A 1: 4000 solution forms numerous small crystals.

Other reagents which give crystals as above are sodium carbonate; potassium chromate; potassium cyanide; sodium phosphate and potassium acetate.

**POTASSIUM FERROCYANIDE.**—The light amorphous precipitates crystallize rather slowly in small, highly polarizing crystals. Many are formed even in the 1: 1000 solution.

**KRAUT'S REAGENT.**—Crystals formed in the two more



### 34 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

dilute solutions from the amorphous precipitate are small and black six-sided plates.

**FERRIC CHLORIDE.**—The amorphous precipitate is slight. Small, highly polarizing crystals are formed in the two more dilute solutions. They appear like those formed with zinc chloride.

**ZINC CHLORIDE.**—Small, highly polarizing crystals are formed in the two more dilute solutions (Plate XXVII, Fig. 1).

**SODIUM PHOSPHOMOLYBDATE.**—Plates of good size are formed in the two more dilute solutions.

**SACCHARIN.**—No amorphous precipitate formed. A few small crystals are formed in the two more dilute solutions. They polarize well. Color reaction: With ammonium vanadate added to dry material a green color is formed, gradually fading to pink; Froehde's reagent gave a blue color.

### CHOLINE

Eight crystalline and seven non-crystalline precipitates were obtained.

**PHOSPHOMOLYBDIC ACID.**—This is a sensitive test for choline. Amorphous precipitates and crystals are formed in all the solutions. They are small, as a rule. The best concentration is 1:200, in which solution great numbers of needles, often in rosettes, are formed. These crystals are often in dense masses (Plate XXIV, Fig. 2).

**SILICO-TUNGSTIC ACID.**—Heavy precipitates form in all the solutions and the best crystals are formed in the 1:500 solution. The crystals are rods or needles, often curved, and normally have a peculiar granular appearance on the surface.

**PHOSPHOTUNGSTIC ACID.**—Heavy, amorphous precipitates are formed with this reagent and small crystals are formed only in the 1: 50 solution. This is not a satisfactory reagent to use as a test for choline.

**BARIUM NITRATE.**—Great numbers of very small crystals are formed in all solutions. They appear to be very small rosettes.

**MERCURIC CHLORIDE.**—Heavy, amorphous precipitate formed in the 1: 50 solution only. Crystals are formed in all the solutions, though only around edges in the 1: 1000 solution. They are small and polarize slightly and are normally spherical.

**KRAUT'S REAGENT.**—Heavy, amorphous precipitates appeared in the three more concentrated solutions. In the 1: 200 solution, a few long and rather narrow, irregular plates are formed around the edge of the drop only. Rosettes of small plates are formed at once in the 1: 50 solution. They are normally six-sided.

**GOLD CHLORIDE.**—The limit of reaction is about 1: 200. Rosettes of plate-like crystals in 1: 50 solution are formed from the amorphous precipitate. They polarize fairly well.

**MAYER'S REAGENT.**—An amorphous precipitate appears in the 1: 50 solution only, and this crystallizes rapidly into plates which are rather small and often triangular in outline.

#### CINCHONINE SULPHATE

Six crystalline precipitates and twenty-three non-crystalline precipitates were obtained.

**SODIUM CARBONATE.**—This is a very delicate and characteristic test. The crystals are small rosettes and are quickly formed in great numbers in all the solutions. They

## 36 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

are especially good in the 1:1000 solution. They form such a dense mass in the more concentrated solutions that they do not show up so well as they do in the 1:1000 solution. They are dark in appearance and do not polarize brightly (Plate XIV, Figs. 1 (X 150) and 2 (X 300) (8).

Numbers of small needles are formed in a 1:20,000 solution.

Other reagents forming crystals as above although the tests are not so sensitive in all cases, are as follows: Potassium hydroxide; potassium chromate, and potassium cyanide.

POTASSIUM PERMANGANATE.—Not a satisfactory test, as the amorphous precipitate frequently does not crystallize. The amorphous precipitate is very dense in all the solutions. The crystals form slowly and best in the 1:200 solution. They are small plates, usually pointed and often in rosettes. The rosettes are often very dense and are found in great numbers as the solution stands.

POTASSIUM FERROCYANIDE.—Great numbers of small rods in rosettes formed in the 1:1000 solution. Most of the crystals in the 1:200 solution are spherical and show distinct polarization crosses; others are rosettes of plates. In the 1:50 solution the amorphous precipitate is very dense and the few crystals which form at first are like those in the 1:200 solution. The precipitate does not crystallize rapidly, however (8) (15).

### CINCHONIDINE SULPHATE

Nine crystalline and twenty-four non-crystalline precipitates were obtained.

PLATINUM CHLORIDE.—The test is sensitive. A 1:20,000 solution forms a number of small crystals. The

crystals are usually rosettes of plates, sometimes of rods. They are clear-cut, but do not polarize highly. The 1:50 solution is too concentrated for best results (Plate IV, Fig. 4) (8).

**SODIUM PHOSPHATE.**—Dense rosettes of needles are quickly formed in the two more concentrated solutions only. They show distinct polarization crosses (Plate VII, Fig. 5).

**POTASSIUM CYANIDE.**—On standing crystallization takes place slowly from the amorphous precipitate first formed in the three more concentrated solutions. The crystals are dark, appearing in rosettes of needles or spherical aggregates.

**SODIUM BENZOATE.**—The very dense, amorphous precipitate in the two more concentrated solutions crystallizes out into large and dense rosettes of needles. These rosettes grow to a large size and can be plainly seen with the naked eye. Stir the solution for quick results.

**PICRIC ACID.**—The crystals are very slowly formed from the amorphous precipitate. They are good-sized rods in masses.

**POTASSIUM HYDROXIDE.**—Spherical crystals are quickly formed in the 1:500 solution upon stirring. Amorphous precipitates form in the 1:500 and more concentrated solutions. There is no precipitate in the 1:1000 solution (Plate XV, Fig. 3).

**POTASSIUM FERROCYANIDE.**—This is not so sensitive as the above, but the crystals, when formed, are similar. An amorphous precipitate and crystals form in the 1:50 solution only.

Sodium carbonate reacts like the above (8).

**POTASSIUM CHROMATE.**—The light, amorphous pre-

### 38 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

precipitate first formed crystallizes into great numbers of rod-shaped rosettes in the 1:1000 solution. There is no precipitate at greater dilutions.

#### COCAINE HYDROCHLORIDE

Ten crystalline and fourteen non-crystalline precipitates were formed.

The following observations were noted concerning the various reactions with cocaine in which crystals were produced.

**GOLD CHLORIDE.**—This is the most sensitive reaction for cocaine. An amorphous precipitate is first produced in all solutions. The crystals are characteristic and a few small ones are produced in a dilution of 1:20,000. The crystals can best be described by photograph. They are normally delicate and characteristic rosettes. When formed slowly they are long rods with many short arms running out at nearly right angles from the main axis. Their shape varies greatly according to the concentration (Plate I, Figs. 5 and 6) (4) (8) (10).

**PLATINUM CHLORIDE.**—This is also a very sensitive test for cocaine and a characteristic one. Feathery crystals are formed up to a dilution of about 1:4000 (Plate IV, Fig. 5) (8) (4) (10) (18).

**PICRIC ACID.**—This is a comparatively poor reagent, as the heavy, amorphous precipitates crystallize with difficulty and usually very slowly. Crystals formed in solutions up to about 1:800, but they are not very characteristic. They are rosettes or sheaves of needles (Plate XIX, Fig. 2) (4) (6) (10) (11).

**POTASSIUM PERMANGANATE.**—Solutions up to about 1:700 give purple-colored plates or aggregates of plates.

Vigorous stirring of the solution is often necessary to start crystallization, which then proceeds rapidly. To obtain this test readily, add only a very small amount of the reagent (Plate XXIII, Fig. 4) (5) (7) (15).

**PALLADOUS CHLORIDE.**—The crystals formed are characteristic, but this reagent is not so sensitive as some of the others mentioned above. The crystals vary much in form according to the conditions of precipitation. One of the most common forms is that obtained with a 1:100 solution, when feathery crystals are produced; 1:500 is about the limit of reaction. For quick crystallization, add a drop of chlorine water or a drop of dilute hydrochloric acid to the solution and then add the palladous chloride and stir with a glass rod. This reaction is of interest, as it was the first one we used and was the starting-point of this investigation (Plate VI, Fig. 4).

**CHROMIC ACID.**—This test is made by adding a small drop of chromic acid solution to the test drop. A precipitate is formed which on stirring disappears. A small drop of strong hydrochloric acid is added and a yellowish deposit is produced, which after stirring on the slide should in a few minutes be transformed into loose, spherical clusters of an acicular crystal. This test appears to be one of the most uncertain because of the difficulty with which crystals are produced (Plate XXII, Fig. 3).

Potassium dichromate may be substituted for the chromic acid in the above.

In this test it was found that after once having obtained crystals no difficulty was experienced thereafter, no matter how many times the test was tried. There is always considerable difficulty in first obtaining crystals. After some time the conclusion was arrived at that the glass rod used

#### 40 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

in making the tests serves to carry at least a trace of crystalline matter from one test to the other, and that this trace causes the whole drop to crystallize out very quickly. This fact is mentioned here to call attention to the necessity of washing the stirring rod thoroughly, since simply drying on a towel will not clean it perfectly.

**FERRIC CHLORIDE.**—The crystals are aggregates of rather coarse, blade-like forms with chisel-shaped ends. This is not a very sensitive test. Stir to obtain quick results (Plate III, Fig. 6).

**POTASSIUM HYDROXIDE.**—In concentrated solutions this reagent produces a white, amorphous precipitate which changes into crystals on standing, or by stirring with a glass rod. The crystals are rod-shaped (4).

Sodium carbonate gives results similar to the above (4) (8).

Potassium cyanide forms large rods from the amorphous precipitate in the 1:50 solution slowly.

In practical work the gold chloride and the platinum chloride tests have been used almost entirely, as they are the most satisfactory.

Tests were performed to determine the effect on the gold chloride test of the presence of another alkaloid with the following results: As a rule, when there is present one-fifth as much of the other alkaloid as of cocaine, it has no effect on the test; one-half the amount affects the crystals in more than half the combinations tried and twice the amount destroys the test in nearly every case.

Other alkaloids in equal amount have a slight effect only on the picric acid test, but change the form of crystals with platinum chloride in most cases.

The potassium permanganate test is destroyed in about one-half of the cases, when an equal amount of another alkaloid is present.

The potassium hydroxide test is spoiled in only eight out of forty cases when another alkaloid is present in equal amount.

The effect of glycerine upon the different tests was tried and it was found that glycerine, when present in one hundred times the amount of the alkaloid, did not interfere with the test in any case.

Likewise granulated sugar present one hundred or more times the amount of the cocaine does not interfere with the tests.

Tannic acid, when present in equal amount with the cocaine, affects the test in all cases.

Gum arabic or lactose solutions do not affect the tests for cocaine in any case.

### CODEINE

Solutions of codeine sulphate were used. The crystalline precipitates number nine; the non-crystalline eleven.

**MARME'S REAGENT.**—This, the best test for morphine, is also the best test for codeine. First we have an amorphous precipitate and from this great numbers of small, silvery-appearing masses are formed at once, even in solutions as dilute as 1:2000. In the more concentrated solutions, such as the 1:200 solution, for example, these masses soon start to crystallize and crystallization spreads rapidly over the field and the crystals appear as small rods in masses. Fig. 1 shows first stages of crystallization, while Fig. 2 shows very little of the precipitate which has not



## 42 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

crystallized. On still further standing, rosettes of good-sized plates, normally very irregular in outline, are formed, although we often have rods in rosettes instead of plates. These changes are well shown by photographs (Plate XVII, Figs. 1, 2 and 3).

Reactions with Mayer's reagent are similar to above (10).

**MILLON'S REAGENT.**—This reagent forms a precipitate in the 1:1000 solution, but no crystals were noted. In the 1:50 solution a precipitate is formed first and it crystallizes in small, spherical crystals. In the 1:200 and more concentrated solutions the precipitate takes on a yellow color and the crystals are still small and spherical. This reaction is of no value as a test, the crystals being too small (Plate XXVI, Fig. 2).

**CHROMIC ACID.**—The amorphous precipitate first formed quickly changes into oil-like drops. Crystals are formed only in the 1:50 solution. They are characteristic, dark in appearance, and are normally spherical, or rosettes of plates. Sometimes they are much larger and bushy in appearance. Formation of crystals takes place slowly unless the drop be stirred (Plate XXII, Fig. 4).

**POTASSIUM CHROMATE.**—This reagent is not sensitive as a test. The 1:50 solution crystallizes out instantly into beautiful, large rosettes. The branches are broad, plate-like, or rods, and have pointed ends (Plate XXI, Fig. 4) (1).

**ZINC-CHLOR-IODIDE.**—The limit of reaction for crystals is about 1:500, but the solution is too dilute for good-sized crystals. Great numbers of rosettes are formed in the 1:50 solution, some being coarse, others made up of needle-like forms (Plate XXVII, Figs. 2 and 3).

**POTASSIUM IODIDE.**—This reagent forms long, needle-like crystals, often in masses, in the 1:50 solution only. Crystals are formed without a first amorphous precipitate (Plate XVIII, Fig. 3) (1).

**WAGNER'S REAGENT.**—This reagent forms precipitates in all solutions, but crystals are formed only in the 1:50 and 1:200 solutions. They are rosettes of plates, light brown in color and usually of large size (Plate X, Fig. 6) (8) (18) (1).

**AMMONIUM THIOCYANATE.**—Limit of reaction about 1:100. Large rosettes consisting of rods are formed in the 1:50 solution. These rods are pointed at the ends. They polarize brightly (Plate XXV, Fig. 2).

#### COLCHICINE

The aqueous solutions are yellow.

No crystalline precipitates were obtained.

Upon adding Wagner's reagent to the 1:50 solution of the alkaloid, an amorphous precipitate is formed. Some very fine needles are formed from this after it stands for some time, but their formation is not always certain.

#### CONIINE

Seven crystalline and nine non-crystalline precipitates were obtained.

**PHOSPHOTUNGSTIC ACID.**—This is a good and sensitive test. Short rods are instantly formed even in a 1:10,000 solution (Plate XXIV, Fig. 5) (13).

**KRAUT'S REAGENT.**—Heavy, amorphous precipitates are first formed. The crystals are small, clear-cut plates of a deep, reddish-brown color, and are often six-sided, but

#### 44 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

are not all of the same shape. Great numbers are formed from the precipitate in the 1: 500 solution and all of the 1: 1000 solution crystallizes. Crystals were also obtained in a 1: 3000 solution (8) (13).

**MARME'S REAGENT.**—The amorphous precipitate is heavy in all cases. On standing it takes on an appearance similar to oil globules, and after some time crystals are formed. They are large and coarse in appearance and form very slowly. They are normally a bundle of rods or plates.

The growth of the crystals may be very clearly seen under the microscope as the drops come in contact with the crystal. The 1: 200 and 1: 500 solutions are best for crystal formation (Plate XVII, Fig. 4) (13).

**MAYER'S REAGENT.**—Amorphous precipitates formed in all the solutions. Crystals are of good-sized rosettes of irregular rods. Crystallization is slow and no crystals are formed in the 1: 1000 solution.

**PHOSPHOMOLYBDIC ACID.**—Many of the crystals formed are small and spherical, others are plate-like, sharply cut, and deep yellow in color. The crystals are formed rather quickly from the amorphous precipitate and are best seen around the edges of the heavy amorphous precipitate and in the more concentrated solutions (13).

**PALLADOUS CHLORIDE.**—Only on stirring do we get crystals. These are small and form only as the solutions become concentrated. They are short rods, often in rosettes.

**BARIUM NITRATE.**—Rosettes of small rods are formed in all the solutions on stirring (13).

The heavy, amorphous precipitate with gold chloride takes on a violet color at once in the 1: 50 solution.

## CORYDALINE

Six crystalline and twenty-seven non-crystalline precipitates were obtained.

**POTASSIUM HYDROXIDE.**—Amorphous precipitates appear in all the solutions. Crystallization is slow. The crystals are rosettes of rods in the 1: 50 solution. In the more dilute solutions, plates or rosettes of plates are formed.

Ammonium hydroxide gives results similar to the above.

**SILVER NITRATE.**—Short rods are formed from the amorphous precipitate in the 1: 50 solution only.

**AMMONIUM THIOCYANATE.**—Small rosettes are formed in all the solutions quickly from the amorphous precipitates.

**POTASSIUM CHROMATE.**—Very fine rods or needles in rosettes are formed in the two more concentrated solutions only.

**MERCURIC CHLORIDE.**—Amorphous precipitates appear in all the solutions and they all crystallize, though not rapidly. Rosettes of rods, polarizing fairly well, is the normal form (Plate VIII, Fig. 2).

**MILLON'S REAGENT.**—In the 1: 50 solution, crystals in rosettes of rods are formed from the amorphous precipitate.

The following color reactions were noted: Light blue quickly changing to dark blue color with Froehde's reagent in the 1: 50 and 1: 200 solutions, and this color gradually fades out. A slight reddish or pink coloration formed with ammonium vanadate in all the solutions up to the 1: 1000. It is very faint in the 1: 1000 solution.

## CYTISINE HYDROCHLORIDE

Nine crystalline and seven non-crystalline precipitates were obtained.

**MAYER'S REAGENT.**—This is the best test for cytisine.

This is a very sensitive test, as good-sized rosettes of rods are soon formed in a 1: 6000 solution. A very dense crystalline precipitate is formed at once in all solutions. They are moss-like, often turning to rods on standing.

**MARME'S REAGENT.**—There are no precipitates in the two more dilute solutions.

An exceedingly dense mass of rods formed very quickly from the amorphous precipitate in the 1: 50 solution. Stir the 1: 200 solution for quick crystallization.

**PLATINUM CHLORIDE.**—This reagent forms crystals only on stirring the 1: 50 solution. They are large and dense rosettes of needles and do not polarize (8).

**PHOSPHOTUNGSTIC ACID.**—This reagent forms heavy, amorphous precipitates in all the solutions, and crystals in all except the 1: 50 solution are formed slowly. They are rosettes of plates and polarize but slightly.

**WAGNER'S REAGENT.**—This is a sensitive test. The amorphous precipitate crystallizes in all the solutions used. The crystals are normally long rods, often in rosettes. They do not polarize. They are often leaf-like rosettes in the 1: 50 solution, and crystallization takes place more slowly in this solution than in the more dilute ones. The crystals grow to a good size in the 1: 1000 solution (Plate XI, Fig. 1).

**PICRIC ACID.**—No crystals appear in any solution more dilute than 1: 200. On stirring the 1: 200 solution we get great numbers of needles or often plates. The 1: 50 solu-

tion crystallizes out slowly, forming very large, dense rosettes of rods (Plate XIX, Fig. 3).

**MERCURIC CHLORIDE.**—Fine rosettes of plates are formed in the two more concentrated solutions. They polarize well. Only a few small ones form on stirring the 1: 500 solution (Plate VIII, Fig. 3).

**GOLD CHLORIDE.**—The best crystals with this reagent are at a concentration of about 1: 200. The crystals are then large, somewhat leaf-like and characteristic. They do not polarize.

A great number of very small crystals are formed on stirring the 1: 1000 solution (Plate II, Fig. 1) (8).

The following color reaction was noted:

The 1: 50 solution takes on a deep reddish-brown color with ferric chloride.

#### DIONINE (ETHYL-MORPHINE)

Eight crystalline and fourteen non-crystalline precipitates were obtained.

No very sensitive tests for dionine were obtained.

**WAGNER'S REAGENT.**—The dense precipitate in the 1: 50 and 1: 200 solutions crystallize rather rapidly into large rosettes of rods. Crystals were not obtained in the more dilute solutions. These crystals are characteristic (Plate XI, Fig. 2) (18).

Kraut's reagent forms crystals similar to the above, but the reagent does not appear to be so sensitive.

**MAYER'S REAGENT.**—The crystals, formed in the two more concentrated solutions, are small. They are silvery in appearance and do not polarize. They form slowly, as a rule, and most of the heavy, amorphous precipitate does not crystallize.

## 48 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Marme's reagent gives results as above.

**ZINC-CHLOR-IODIDE.**—This reagent forms a heavy precipitate and in the 1:50 solution a few small crystals form around the edge. They do not polarize and might easily be overlooked.

**SODIUM CARBONATE.**—Short rods or rosettes of rods are formed in the 1:50 solution only and are formed slowly unless the drop be stirred. No precipitate formed (Plate XIV, Fig. 3).

Potassium hydroxide gives results as above.

**MERCURIC CHLORIDE.**—No precipitate appeared in the two more dilute solutions. An amorphous precipitate formed in the 1:50 solution only. In the 1:200 and more concentrated solutions, large rosettes of plates are the normal form. Stir the 1:200 solution in order to get quick crystallization (Plate VIII, Fig. 4).

### ECGONINE HYDROCHLORIDE

Three crystalline and four non-crystalline precipitates were obtained.

**PHOSPHOMOLYBDIC ACID.**—This is a delicate and characteristic test. Crystalline precipitates are formed in all solutions up to 1:4000. They are best at a dilution of 1:500. All of the amorphous precipitate in the 1:500 solution does not crystallize until it stands for some time. The crystals are dense rosettes of needles often of large size. They do not polarize highly.

**PHOSPHOTUNGSTIC ACID.**—The crystals are very small and indistinct rosettes and are best seen in the 1:1000 solution. The amorphous precipitates in the more concentrated solutions do not crystallize.

**KRAUT'S REAGENT.**—Heavy, amorphous precipitates

are formed. Crystals are formed in the 1:200 and in the 1:500 solutions only. They are six-sided and not very large and are clear-cut plates (Plate XIII, Fig. 3).

### HEROINE (DIACETYL MORPHINE)

Seven crystalline and nineteen non-crystalline precipitates were obtained.

No very sensitive tests were obtained on heroine.

**SODIUM CARBONATE.**—A rather light, amorphous precipitate is formed in the 1:200 solution and it crystallizes slowly. Crystals polarize very highly and are often fine rosettes of pointed plates. There was no precipitate in the dilute solution.

**SODIUM PHOSPHATE.**—This reagent forms rather coarse rosettes of rods in the 1:50 solution only, and no first amorphous precipitate appeared.

**POTASSIUM HYDROXIDE.**—No precipitate appears except in the 1:50 solution, and this soon crystallizes. The crystals are rosettes of rods, often not well formed.

**PLATINUM CHLORIDE.**—Crystals are formed only from the heavy precipitate in the two more concentrated solutions after some time. They are spherical or often fine rosettes of needles and do not polarize (18).

**MERCURIC CHLORIDE.**—No precipitate appears in the dilute solutions. In the 1:200 solution a few crystals are slowly formed from the slight precipitate. They do not polarize brightly. In the 1:50 solution we have a dense precipitate. Crystals are rather slowly formed, but they grow into good-sized rosettes, sometimes of blade-like forms. The reaction resembles that of morphine with this reagent; hence, if it is obtained, apply the tests for morphine, especially with Mayer's and Marme's reagents. The



## 50 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

amorphous precipitate appears like oil globules before it crystallizes (Plate VIII, Fig. 5).

**POTASSIUM CYANIDE.**—In the 1:50 solution, a rather dense precipitate crystallizes slowly into solid, jagged-appearing crystals, often rods or cubes. Beautiful rosettes are often formed. By stirring the 1:200 solution we get great numbers of plates polarizing very brightly (Plate XXI, Fig. 2).

**PICRIC ACID.**—Crystals appear in the two more concentrated solutions from the heavy amorphous precipitates. They are spherical or often small rosettes, and do not polarize brightly (Plate XIX, Fig. 4).

### HOMATROPINE

Four crystalline and fourteen non-crystalline precipitates were obtained.

**GOLD CHLORIDE.**—The limit of reaction is about 1:500, as the 1:1000 solution forms neither crystals nor amorphous precipitate. In the 1:500 solution a slight amorphous precipitate is first formed. This, on standing, turns into oil-like drops and from these crystals are formed. They form slowly, are of a greenish color, and polarize brightly. They are rosettes of plates. In the 1:200 solution the amorphous precipitate is considerably heavier than before and crystallization is slow. The crystals sometimes appear to be of an orange color. Even in the 1:50 solution crystallization is very slow (Plate II, Fig. 2) (17).

**WAGNER'S REAGENT.**—This is a sensitive test, as a number of very small crystals form in a 1:4000 solution on standing, though they are too small to be of service as a test.

The amorphous precipitate in the 1:1000 solution is dense. The crystals form slowly. They are nearly all small and dark-brown in color and are mainly six-sided. A few are larger and consist of several radiating branches. They vary in color, being black, light or dark-brown, yellow, and often of a green color. The photographs show the decided difference in the appearance of these crystals (Plate XI, Figs. 3 and 4) (17).

Kraut's reagent forms crystals quite similar to above.

MILLON'S REAGENT.—Small spherical crystals are formed in the 1:50 solution only (Plate XXVI, Fig. 3).

#### HYDRASTINE

Thirty-three amorphous precipitates were obtained with this alkaloid and only one crystalline precipitate.

POTASSIUM HYDROXIDE.—Upon adding a 25 per cent. solution of this reagent to the 1:1000 solution of the alkaloid and stirring, crystals are produced from the amorphous precipitate. They are clear-cut rosettes.

Crystal formation is much slower if the solution is not stirred. The crystals are similar but larger in more concentrated solutions.

No crystals were obtained with a 5 per cent. solution of potassium hydroxide, and it is often difficult to obtain any crystals at all even with the 25 per cent. solution (Plate XV, Fig. 4).

The following color reaction was noted: Ammonium vanadate gives a pink color which is not permanent in the 1:50 solution.

Ammonium thiocyanate gives an amorphous precipitate in the 1:50 solution only.

## HYDRASTININE

All the solutions showed fluorescence, especially the more dilute ones.

Eight non-crystalline and eleven crystalline precipitates were obtained.

POTASSIUM PERMANGANATE.—The crystals formed with this reagent are large and characteristic. The amorphous precipitate which is first formed does not ordinarily crystallize in the 1:1000 solution. Sometimes we get a few rods and plates. In the three more concentrated solutions, however, we get great numbers of large plates often in rosettes. They have saw-tooth edges or often appear like some very deeply cut leaves (Plate XXIII, Fig. 5) (15).

GOLD CHLORIDE.—This reagent forms amorphous precipitates in all the solutions, and the two more concentrated solutions crystallize only on stirring. The crystals formed are rods, often pointed or notched at the ends and sometimes occurring in rosettes.

MERCURIC CHLORIDE.—On stirring the 1:1000 solution we get a few small rods. Rods, often pointed, and in rosettes quickly formed on stirring the 1:500 solution. A dense mass of large rods instantly formed in the 1:200 solution. The 1:50 solution crystallizes out into one dense mass of crystals (15).

CHROMIC ACID.—This test is characteristic but not very sensitive, as no crystals are formed at greater dilutions than 1:200. In the more concentrated solutions we get great numbers of crystals. They are normally dense rosettes of rods of peculiar shape, often pointed. Variations in the appearance of the crystals are shown in the photographs.

In the 1:50 solution great numbers of large moss-like rosettes are formed at once from the amorphous precipitate (Plate XXII, Figs. 5 and 6).

**PICRIC ACID.**—Picric acid forms crystals in the two more concentrated solutions only. They are plates or rosettes of plates. In the 1:500 solution they are often eight-sided; some are irregular in outline. They are normally rosettes of large size in the more concentrated solutions and polarize brightly (Plate XIX, Fig. 5) (16).

**ZINC-CHLOR-IODIDE.**—Amorphous precipitates are heavy and numbers of crystals are formed quickly, especially in the 1:1000 solution if stirred. The crystals are needles or rods usually pointed and often in rosettes.

**PALLADOUS CHLORIDE.**—No precipitate appears in the 1:1000 solution.

Numbers of rosettes are formed in the 1:500 solution. They are composed of sharp-pointed needles resembling thorns.

In the 1:200 solution we have large crystals in two forms, needles in rosettes and rosettes of plates. In the 1:50 solution we get a dense mass of needle-shaped crystals. Rosettes of plates are not so common (Plate VI, Fig. 5).

**PLATINUM CHLORIDE.**—Crystals form only on stirring in the 1:1000 and 1:500 solutions, and they are rosettes of rods, as a rule. The dense precipitates in the other two solutions crystallize quickly into large, bushy crystals (Plate IV, Fig. 6).

**MAYER'S REAGENT.**—The precipitates are all heavy with this reagent and crystals are formed only on stirring. They are very small in all except the 1:1000 solution, and in this solution they are often good-sized rosettes of rods.

**MARME'S REAGENT.**—Amorphous precipitates appear which crystallize without stirring in all solutions. A dense mass of crystals are obtained in the two more concentrated solutions. The crystals in the 1:1000 solution are large and polarize highly. They normally have cross arms and jagged edges.

**AMMONIUM MOLYBDATE.**—Heavy, amorphous precipitates and great numbers of small needle-shaped crystals are formed in all the solutions.

#### HYOSCYAMINE HYDROBROMIDE

An alkaloidal salt labeled "Daturine Sulfate" gave same results as the one labeled hyoscyamine hydrobromide, and the chemical determinations were made on the former.

Six crystalline and fifteen non-crystalline precipitates were obtained.

**KRAUT'S REAGENT.**—The heavy, amorphous precipitate crystallizes slowly into irregular rods in the 1:500 and 1:1000 solutions. Crystals are larger and more quickly formed in the more concentrated solutions. They are often in rosettes.

**GOLD CHLORIDE.**—This is not a sensitive test. Amorphous precipitates appear in all the solutions. Crystals of pointed rods or irregular plates, often in rosettes, are formed in the 1:50 solution after some time and on stirring (Plate II, Fig. 3).

**MERCURIC CHLORIDE.**—An amorphous precipitate forms in the 1:50 solution only.

Crystals appear only in the two more concentrated solutions. They are large rosettes of rods polarizing brightly. Stir the 1:200 solution for quick results.

**PICRIC ACID.**—Dense rosettes of needles are formed

slowly upon stirring the two more concentrated solutions only.

**WAGNER'S REAGENT.**—Heavy, amorphous precipitates in all the solutions and small crystals are quickly formed. Some look like those formed with atropine and this reagent. They are, as a rule, larger than those formed with atropine. In the 1:50 solution, besides this form, we have large crystals of a light-green color and which are dense rosettes usually moss-like in general appearance (Plate XI, Fig. 5). Small crystals are formed in a 1:2000 solution.

**ZINC-CHLOR-IODIDE.**—A gelatinous precipitate formed in all the solutions. The crystals are small plates and similar to those formed with atropine.

## THE OPIUM ALKALOIDS

The following opium alkaloids were studied: Morphine, codeine, apomorphine, apocodeine, narcotine, narceine, papaverine, thebaine, peronine, dionine and heroine. Several of these alkaloids have already been discussed.

### MORPHINE

Four aqueous solutions of morphine hydrochloride were used, the alkaloid being present one part to 1000, 500, 200, and 50, respectively. Eleven non-crystalline and eleven crystalline precipitates were obtained with these solutions.

**MARME'S REAGENT.**—This is the best test for morphine. In all the solutions except the 1:1000 a gelatinous precipitate is formed which crystallizes out quickly. This precipi-

## 56 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

tate has a silvery appearance under the microscope. These crystals are rosettes of very fine needles and are characteristic. They form a dense mass, especially so in the more concentrated solutions. In the 1:1000 solution we get no precipitate, but by adding a drop of the reagent and allowing to stand for a short time, long needles form around the edge of the drop (Plate XVII, Fig. 5).

**WAGNER'S REAGENT.**—A very characteristic test, though not so sensitive as the one with Marme's reagent. A heavy, amorphous precipitate is formed in all solutions. This precipitate forms reddish-brown drops before crystallization takes place, and from the precipitate crystallization takes place very slowly.

It is often necessary to allow the solution to stand several minutes before crystals are formed. The crystals are large plates, reddish-brown in color, and irregular in outline. Optimum concentration is about 1:200. While the crystals are normally as described, yet we often obtain rosettes of fine needles in the 1:50 solution, or sometimes rods. These crystals are not dark-brown in color, but are light in appearance and similar to those formed by the potassium iodide solution. Stir with a glass rod about thirty strokes as soon as reagent is added to 1:50 solution if quick crystallization be desired. These crystals are not so large and are usually more regular in outline than when they form more slowly (Plate XI, Fig. 6) (18).

**SODIUM CARBONATE.**—Great numbers of small crystals formed in the 1:200 solution, without the formation of an amorphous precipitate. These crystals are characteristic, being sharply defined rods often in rosettes. Crystals formed in more concentrated solutions than this are fine, clear-cut, and characteristic, though not large. The

solutions must be stirred for quick crystallization. No precipitate occurs in solutions more dilute than the 1:200 (Plate XIV, Fig. 4) (8).

**MAYER'S REAGENT.**—A gelatinous precipitate, with a silvery appearance under the microscope, is formed, but since we have not been able to prove that crystals are formed, the appearance is best described by the photograph (Plate XVI, Fig. 3). Barium-mercuric-iodide gives results similar to above. As the reactions with codeine are quite similar to this, these reagents are only of value in distinguishing morphine and codeine from other alkaloids.

**OTHER TESTS.**—The other tests for morphine are not sensitive and have not been found of practical value. They are briefly as follows:

Potassium chromate forms rods or rosettes of rods only on stirring the 1:200 and more concentrated solutions. This reaction is not at all sensitive, as it is often difficult to obtain crystals on stirring the 1:200 solution (Plate XXI, Fig. 5) (4).

Zinc-chlor-iodide forms a slight gelatinous precipitate, but no crystals in the 1:200 solution, and a dense precipitate which crystallizes instantly in two forms of crystals in the 1:50 solution. Yellow-brown, shiny crystals are usually common and these do not polarize. A dense mass of needle-like crystals is also formed around the edge of the drop. These latter, judging from their appearance, are formed by the potassium iodide in the reagent.

Mercuric chloride forms large rosette-like crystals in the 1:50 solution only and very quickly when stirred. These crystals are formed without an amorphous precipi-



tate being thrown down first and are normally dense rosettes of rods (Plate VIII, Fig. 6) (8).

Potassium iodide forms needles in the 1:50 solution only and slowly. These needles are normally long and in rosettes, and may often be easily seen without the aid of the microscope (Plate XVIII, Fig. 4).

Kraut's reagent forms very heavy, amorphous, brick-red precipitates in all solutions. Crystals are formed in the 1:50 solution only, and are few and small and formed from the precipitate, but only a very small part of the precipitate crystallizes. The crystals are very small rods and so infrequently formed that this reagent is worthless as a test for morphine.

Potassium permanganate. A dense mass of very small crystals noted in more concentrated solutions only around the edges of the heavy precipitate which is formed. These crystals are irregular in outline and too small to be of service as a test.

#### NARCEINE

Three solutions of narceine hydrochloride were used in dilutions of 1:1000, 1:500, and 1:200.

Nine crystalline and nineteen non-crystalline precipitates were obtained.

**KRAUT'S REAGENT.**—Very dense, amorphous precipitates are first formed. The crystals are beautiful large rosettes of needles and are very characteristic, as they are deep-blue in color. The test is not very sensitive, as the 1:500 solution forms crystals only on standing for some time. No crystals were formed in the 1:1000 solution.

Wagner's reagent gives results similar to the above (Plate XII, Fig. 1) (1).

**POTASSIUM IODIDE.**—The crystals are rosettes of needles of good size, blue in color and formed in small numbers in the 1:500 solution, but many are formed in the more concentrated solutions. The crystals are like those formed with Kraut's solution or with Wagner's reagent (8).

**ZINC-CHLOR-IODIDE.**—Heavy, amorphous precipitates and great numbers of fine, blue rosettes of needles are formed in all but the 1:1000 solution.

**PALLADOUS CHLORIDE.**—Amorphous precipitates formed in the 1:200 solution only. Small rosettes or sheaves of needles are slowly formed in all the solutions (Plate VI, Fig. 6).

**PLATINUM CHLORIDE.**—Beautiful feathery rosettes are formed from the amorphous precipitates in all solutions. This is a sensitive test (Plate V, Fig. 1) (1) (10).

**POTASSIUM CHROMATE.**—No amorphous precipitates appeared. Rosettes of needles are formed in the more concentrated solutions only. Stir with a glass rod for quick crystallization (1) (10).

**PICRIC ACID.**—The 10 per cent. alcoholic solution gave heavy, amorphous precipitates in all the solutions and rosettes of small plates formed only in the 1:50 solution.

**GOLD CHLORIDE.**—While we have a precipitate in all solutions, crystals were only obtained in the 1:50 solution after standing. They are dense rosettes of needles. The photograph shows very clearly the drops in process of crystallization (Plate II, Fig. 4).

**POTASSIUM HYDROXIDE.**—There were no amorphous precipitates, but rosettes of needles formed in the 1:50 solution (Plate XV, Fig. 6).

## NARCOTINE

Solutions of narcotine hydrochloride were used.

Eight crystalline and twenty-six non-crystalline precipitates were obtained.

POTASSIUM HYDROXIDE.—In the 1:1000 solution an amorphous precipitate which is fairly heavy is formed and crystals are slowly formed from this. They are needles.

In the 1:500 solution the precipitate is dense and great numbers of crystals are quickly formed. They are normally rosettes of needles of good size and do not polarize brightly.

In the 1:200 solution the precipitate is very dense and needles in rosettes, or more often in sheaf-like bundles, are formed. The whole precipitate crystallizes out on standing.

In the 1:50 solution the precipitate crystallizes to a dense mass of rosettes of needles on standing.

The following reagents give results practically the same as the above, although there is some variation in sensitiveness of the reactions; potassium acetate (Plate XII, Fig. 5); potassium chromate; potassium cyanide; sodium carbonate (Plate XIV, Fig. 5); sodium phosphate, and sodium phosphomolybdate (8) (2).

The sodium carbonate added to the alkaloid in a solution of 1:20,000 forms a number of very fine needle crystals.

Wormley describes the crystals formed with potassium hydroxide with potassium chromate and those formed with potassium acetate, and gives plates illustrating their normal form.

## NICOTINE

Seven crystalline and eleven non-crystalline precipitates were obtained.

**GOLD CHLORIDE.**—A very heavy precipitate is formed in the 1:1000 solution, and this crystallizes quickly into small spherical or sheaf-like crystals. They polarize poorly. In the 1:500 solution the precipitate and crystals are as above. The crystals do not form as readily in the 1:50 solution as they do at greater dilutions.

This test is sensitive, as an aqueous solution of about 1:15,000 gives considerable numbers of small and characteristic crystals (Plate II, Fig. 5) (8).

**MERCURIC CHLORIDE.**—The amorphous precipitate is very slight in the 1:1000 solution and crystallization is slow unless the solution be stirred, when crystals are formed at once. They are small, clear-cut rosettes of plates and polarize but slightly. In the more concentrated solutions the crystals are larger and form more rapidly.

A 1:4000 solution gives a number of small crystals on stirring (Plate IX, Fig. 1) (1) (8).

**KRAUT'S REAGENT.**—The amorphous precipitate crystallizes at once in needles, often in rosettes, upon stirring the 1:500 solution. No crystals were obtained in the 1:1000 solution.

In the two more concentrated solutions, the crystals are large rods, light-yellow in color and polarize brightly (8).

**WAGNER'S REAGENT.**—Crystals are obtained with difficulty from the heavy, amorphous precipitates, especially if much of the reagent be used. No crystals were obtained in the 1:1000 solution. Use but a small amount of the reagent for satisfactory results.

**MAYER'S REAGENT.**—Great numbers of small, spherical crystals are formed from the amorphous precipitate in the two more concentrated solutions only. A light, amor-

phous precipitate is formed in the 1: 500 solution, but no crystals are formed at this dilution (10).

**PICRIC ACID.**—This is a sensitive test. The crystals are large and form instantly from the heavy, amorphous precipitate in all solutions. The precipitate first formed immediately dissolves unless sufficient of the reagent be used. Some crystals were obtained in the 1: 4000 solution and this is about the limit of reaction (1) (6) (10) (11) (12) (16).

**BARIUM NITRATE.**—Great numbers of small crystals are formed at once and they polarize brightly. They are dumb-bell shaped.

#### PAPAVERINE

Thirteen crystalline and twenty-two non-crystalline precipitates were obtained.

**POTASSIUM HYDROXIDE.**—Amorphous precipitates appear in all the solutions and these precipitates all crystallize on standing and crystallization takes place more slowly in the more concentrated solutions. The crystals are small rods or rosettes of rods often arranged in the shape of a fan. Upon adding this reagent to a 1: 10,000 solution and stirring, a considerable number of small rods are formed at once.

Potassium chromate and also potassium acetate give results similar to the above (Plate XV, Fig. 5).

**SODIUM CARBONATE.**—The amorphous precipitate crystallizes slowly unless stirred. On standing, large rosettes of rods are formed, while on stirring the crystals are in small rods only.

Sodium phosphate gives crystals similar to the above.

**ZINC CHLORIDE.**—All the solutions crystallize at once. The crystals are normally small rosettes of irregular plates. This appears to be a good test, a few small crystals being formed in a 1:2000 solution. An amorphous precipitate first formed in the 1:50 solution only (Plate XXVI, Fig. 6).

**MERCURIC CHLORIDE.**—Characteristic crystals, though not large ones, are formed with this reagent. They appear to be cubical with rounded edges, or often rosettes of plates in layers. Amorphous precipitates are formed in all the solutions and these crystallize on stirring (Plate IX, Fig. 2) (8).

Other crystalline precipitates are briefly as follows:

**ZINC-CHLOR-IODIDE.**—Crystals formed slowly from the amorphous precipitate. They are normally like crystals formed with zinc chloride.

**PALLADOUS CHLORIDE.**—Small, irregular crystals are formed from the amorphous precipitate in the 1:200 and 1:50 solutions on standing (Plate VII, Fig. 1).

**MAYER'S REAGENT.**—The amorphous precipitate is very dense. The crystals are formed slowly around the edges of the drops and are not characteristic. They are small plates often in dense masses.

**MARME'S REAGENT.**—The amorphous precipitates are all very dense and the crystals are small rosettes of plates and do not form quickly. These crystals appear to better advantage after standing some time, as they grow larger.

**FERRIC CHLORIDE.**—Crystals appear only in the two more concentrated solutions. They are rather quickly formed in great numbers from the amorphous precipitates and appear almost square.

## 64 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

**MILLON'S REAGENT.**—The crystals formed are identical with those formed by the mercuric chloride solution, but Millon's reagent is less sensitive.

### **PERONINE (BENZYL MORPHINE HYDROCHLORIDE)**

Three solutions only were used and they were aqueous solutions of the following strengths: 1:1000, 1:500, and 1:200.

**POTASSIUM IODIDE.**—This is a sensitive and satisfactory test.

Large, dense rosettes of rods or needles are formed from the amorphous precipitates at once. Many good-sized crystals are formed in the 1:1000 solution; a non-crystalline precipitate is not formed first (Plate XVIII, Fig. 5).

**HYDROCHLORIC ACID.**—Upon adding dilute hydrochloric acid solution to the 1:200 solution and stirring, crystals of rods, often in rosettes, are formed. The rods are usually notched at the ends.

Ferric chloride gives crystals in the 1:200 solution only, and they appear like those above.

**BARIUM NITRATE.**—Amorphous precipitates and then crystals are formed in the 1:200 solution only, and they are rods or needles, the rods often being notched at the ends.

Silver nitrate reacts in the same manner as this reagent.

**MAYER'S REAGENT.**—Heavy, amorphous precipitates appear in all the solutions, but crystals are formed from the precipitate only in the 1:200 solution. They are rosettes of rods, forming slowly but growing to a large size.

**AMMONIUM THIOCYANATE.**—Rosettes of rods are rather quickly formed from the heavy, amorphous precipitate in the 1:200 solution and on stirring the 1:500 solution.

## PHYSOSTIGMINE SULPHATE (ESERINE)

Two crystalline and sixteen non-crystalline precipitates were obtained.

No sensitive test for this alkaloid was obtained.

GOLD CHLORIDE.—Amorphous precipitates appear in all the solutions, but crystals only in the 1:50 solution. The crystals are very small and dark in appearance. They are formed in great numbers from the heavy, dark-brown precipitate first produced.

The following color reactions were noted:

Potassium hydroxide gives a deep-pink color in all the solutions.

Ammonium vanadate gives a red color in the 1:50 solution and this fades out quickly. A pink color is obtained in the 1:200 solution.

Potassium cyanide gives a pink color in the solutions on standing.

## PILOCARPIDINE

Three crystalline precipitates were obtained.

PHOSPHOTUNGSTIC ACID.—This is the best test for this alkaloid. Heavy, amorphous precipitates and on stirring great numbers of small rosettes or needle-like crystals are formed. If not stirred the crystals are formed only around the edges of the drops (Plate XXIV, Fig. 6).

PHOSPHOMOLYBDIC ACID.—Very heavy, amorphous precipitates are formed in all solutions. On standing, small spherical crystals are formed. Especially great numbers formed in the 1:50 solution. They do not polarize.

PLATINUM CHLORIDE.—Rosettes of large plates are quickly formed in the 1:50 solution only. No amorphous precipitate or crystals formed in the 1:200 solution (17).



## PILOCARPINE HYDROCHLORIDE

Two crystalline and fourteen non-crystalline precipitates were obtained.

**PLATINUM CHLORIDE.**—The most characteristic crystals were obtained with this reagent. This is not a very sensitive test, as no crystals were obtained in more dilute solutions than 1:200. Upon stirring the 1:200 solution, we get some crystals around the edges. They are rosettes of irregular plates. In the 1:50 solution great numbers of clear-cut plates are formed instantly (Plate V, Fig. 2) (8).

**GOLD CHLORIDE.**—Heavy, amorphous precipitates formed in all but the 1:1000 solution, and these crystallize upon stirring in plates or often in rosettes (10).

## PIPERINE

Solutions in 90 per cent. alcohol were used.

Many reagents are precipitated in crystalline form when added to alcohol, and for this reason alcoholic solutions are not as satisfactory to work with as aqueous or acid solutions.

The crystals formed were in most cases similar, being rods of needles. They were formed with all the following reagents: Mercuric chloride; platinum chloride; sodium nitro-prusside; potassium acetate; potassium ferricyanide; saccharin; potassium iodide; Marme's reagent, and ammonium molybdate.

## THE CINCHONA ALKALOIDS

Microchemical tests were worked out for the following cinchona alkaloids: Quinine; quinidine; cinchonine; cinchonidine, and quinoline. Cinchonine and cinchonidine have already been discussed; see pp. 35 and 36.

## QUININE SULPHATE

Five crystalline precipitates and twenty-seven non-crystalline precipitates were obtained.

No sensitive tests for this alkaloid found.

SODIUM PHOSPHATE.—There was no precipitate in the two more dilute solutions.

Great numbers of large, sheaf-like crystals are quickly formed in the 1:200 solution. In the 1:50 solution we have besides the sheaf-like crystals, another form. These particles are rather small, silvery in appearance, and are present in great numbers. They do not polarize and are probably non-crystalline, their appearance being similar to the particles formed when Mayer's reagent is added to morphine or to codeine (Plate VII, Fig. 6).

POTASSIUM ACETATE.—Dense masses of very fine needle crystals or rosettes of these are formed only in the 1:50 solution (Plate XII, Fig. 6).

POTASSIUM CHROMATE.—No reaction in the two more dilute solutions.

By adding sufficient of this reagent and stirring, we get rosettes of needles at once in the 1:200 solution. In the 1:50 solution the dense precipitate first formed crystallizes rapidly into large rosettes of rods on stirring (Plate XXI, Fig. 6).

WAGNER'S REAGENT.—While dense precipitates are formed in all the solutions, no crystals were obtained in any but the 1:50 solution. In this solution crystallization is slow. The crystals are, as a rule, not large and do not polarize brightly. They are not sharp in outline.

Much of the precipitate takes on a deep rose-red color, this color being different from that obtained with any other alkaloid tested with this reagent (Plate XII, Fig. 2).

## 68 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Kraut's reagent gives reactions similar to the above.

**AMMONIUM THIOCYANATE.**—The amorphous precipitate in the 1:50 solution crystallizes quickly in large, dense, moss-like crystals. The slight precipitate in the 1:200 solution forms small crystals on stirring. The two photographs (Plate XXV, Figs. 4 and 5) show how widely the crystals may vary in appearance.

### QUINIDINE SULPHATE

Six crystalline and twenty-six non-crystalline precipitates were obtained.

**POTASSIUM CHROMATE.**—No precipitates appeared in the dilute solutions. In the 1:50 solution a very dense, amorphous precipitate is first thrown down and crystals are slowly formed. They often exhibit a braided appearance.

**GOLD CHLORIDE.**—In the 1:500 solution, a heavy, amorphous precipitate crystallizes at once on stirring or slowly when not stirred into needles or rosettes of these. These crystals are formed in great numbers. No crystals appear in the 1:1000 solution. Crystals do not form quickly in the more concentrated solutions (Plate II, Fig. 6) (8).

**MERCURIC CHLORIDE.**—No crystals are formed in any solution more dilute than the 1:200. In this solution fair-sized rosettes are formed from the rather dense, amorphous precipitate. These crystals polarize brightly around the edges, but not in the centre (Plate IX, Fig. 3).

**POTASSIUM IODIDE.**—No amorphous precipitate appears in the more dilute solutions. Crystals in great numbers are formed at once on stirring the 1:1000 solution. They are normally triangular in outline.

A few crystals were formed in a 1:2000 solution. In

the more concentrated solutions the crystals are large and form quickly. This reagent does not form crystals with any other of the cinchona alkaloids studied (Plate XVIII, Fig. 6) (8).

**POTASSIUM FERROCYANIDE.**—Great numbers of rods are formed quickly in the more concentrated solutions. Their appearance is best described by the photograph. No precipitate appears in the 1:1000 solution (Plate XX, Fig. 3) (8).

**AMMONIUM THIOCYANATE.**—Small rosettes form on stirring a 1:1000 solution. Very large rosettes appear in all the more concentrated solutions (Plate XXV, Fig. 3).

#### QUINOLINE

Eleven crystalline and seventeen non-crystalline precipitates were obtained.

**CHROMIC ACID.**—This is not a sensitive test, as crystals were obtained only in the 1:50 solution. They are rosettes of leaf-like forms and polarize brightly. The amorphous precipitate is light and crystallizes slowly (Plate XXIII, Fig. 1).

**GOLD CHLORIDE.**—This is a sensitive test. The 1:1000 solution crystallizes out quickly into a dense mass of crystals of a green color, appearing like some form of sea-weed. The 1:500 solution is too concentrated to give the best results. Some fair-sized needles are formed in a 1:5000 solution (Plate III, Fig. 1).

**PLATINUM CHLORIDE.**—Needle-like crystals, often in rosettes, are obtained on stirring the 1:1000 solution. In the 1:50 solution the crystals are in a dense mass and small (Plate V, Fig. 3) (8).

**MERCURIC CHLORIDE.**—The crystals are dense rosettes

## 70 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

in all solutions except the 1: 1000, in which solution there is no precipitate (Plate IX, Fig. 4) (8).

**WAGNER'S REAGENT.**—Heavy, amorphous precipitates and crystals are slowly formed in all the solutions. They are rods and vary from brown or light yellowish-brown to a dark-bluish color (Plate XII, Fig. 3).

**KRAUT'S REAGENT.**—In the 1: 1000 solution the amorphous precipitate crystallizes out quickly in beautiful reddish-brown rosettes of needles. A 1: 8000 solution gave a few very small crystals. The more concentrated solutions do not give any more satisfactory results than the 1: 1000 solution (Plate XIII, Fig. 4) (8).

**PICRIC ACID.**—This is a sensitive test for quinoline. Large crystals are formed instantly in the 1: 1000 solution, and a very dense mass of crystals in the more concentrated solutions. A few small crystals are formed in a 1: 3000 solution (Plate XIX, Fig. 6).

**MAYER'S REAGENT.**—The precipitate in the 1: 1000 or 1: 50 solution does not crystallize. The crystals are normally large rods in the other two solutions.

**POTASSIUM FERROCYANIDE.**—The crystals are small rods or four-sided plates with sharp angles and formed only in the two more concentrated solutions. The amorphous precipitate is very slight in the 1: 500 solution (Plate XX, Fig. 4) (8).

Potassium ferrocyanide reacts like the above.

**MILLON'S REAGENT.**—The crystals are small, dark rosettes and formed in the two more concentrated solutions only. They have a light-pink color when in masses and this color is especially to be seen in the 1: 50 solution (Plate XXVI, Fig. 4).

SCOPOLAMINE HYDROBROMIDE (HYOSCINE  
HYDROBROMIDE)

Samples marked either "Hyoscine" or "Scopolamin" give identical microchemical reactions. Only three crystalline precipitates were obtained. Thirteen non-crystalline precipitates were obtained.

**GOLD CHLORIDE.**—This is a sensitive test and the only one, apparently, of practical value. The crystals are instantly formed on stirring the solutions, otherwise they form slowly. Numbers of small crystals are formed in a 1:4000 solution on stirring. They are triangular in outline. The crystals grow to a large size, especially in the 1:200 solution. They polarize brightly and are yellow in color and normally are rosettes of plates with coarse, saw-tooth edges. They are characteristic. Amorphous precipitates appear in all the solutions up to 1:500 (Plate III, Fig. 2) (7).

**KRAUT'S REAGENT.**—The precipitates are all dense. On standing they all crystallize. They are noticed especially around the edges and are usually rosettes of rods.

**WAGNER'S REAGENT.**—Crystals are very slowly formed from the heavy, amorphous precipitates. On stirring a sticky mass is formed from the amorphous precipitate and this on further stirring crystallizes rapidly into short rods, sometimes in rosettes (Plate XII, Fig. 4).

## SOLANINE

No satisfactory test was obtained on this substance. Twenty-seven amorphous precipitates were obtained.

## SPARTEINE SULPHATE

Seven crystalline and fifteen non-crystalline precipitates were obtained.

**GOLD CHLORIDE.**—The only very sensitive test is that with gold chloride. A great number of small, blade-like crystals which polarize fairly well are formed in the 1: 1000 solution. The crystals are larger but similar in shape in the 1: 500 solution. In the two more concentrated solutions the crystals vary greatly in shape and size and are often in masses (Plate III, Fig. 3) (10).

**ZINC-CHLOR-IODIDE.**—Very small crystals were formed in all the solutions, but the greater part of the precipitate does not crystallize. On standing, the crystals in the 1: 1000 solution grow to a fair size. They are very irregular in outline.

**PALLADOUS CHLORIDE.**—No amorphous precipitates appear. On standing, fine, large, spherical crystals or rosettes are formed in the 1: 50 solution and a few in the 1: 200 solution. They are of a deep, reddish-brown color (Plate VII, Fig. 2).

**POTASSIUM FERRICYANIDE.**—This is not sensitive as a reagent for sparteine. Large plates and many small square ones are formed in the 1: 50 solution only.

**MARME'S REAGENT.**—The dense, amorphous precipitates crystallize slowly on standing, great numbers of crystals being formed. They are rather slender rods and of good length.

**FERRIC CHLORIDE.**—Great numbers of crystals are formed around the edge of the drop in the 1: 50 solution and a few in the 1: 200 solution. They float on the liquid.

**SILVER NITRATE.**—Crystals are formed in great numbers on stirring the 1: 50 solution only. They are normally small rods and polarize brightly.

## STRYCHNINE SULPHATE

Twenty-seven crystalline and five non-crystalline precipitates were obtained with this alkaloid.

Many sensitive and characteristic tests were worked out.

POTASSIUM HYDROXIDE.—Rods normally with a V-shaped recess in each end are formed in all the solutions. A few small crystals are formed in a 1:20,000 solution. The crystals are large and rough in appearance in the two more concentrated solutions and are formed from the amorphous precipitates first thrown down. Stir the more dilute solutions for quick crystallization (Plate XVI, Fig. 1) (8) (1).

Crystals similar to the above are formed with ammonia and also with sodium carbonate (Plate XIV, Fig. 6) (8).

SODIUM NITRO-PRUSSIDE.—No precipitates were obtained in the two more dilute solutions.

A very slight precipitate appeared in the 1:200 solution and this crystallized slowly. The crystals are spherical and show distinct polarization crosses. In the 1:50 solution the dense, amorphous precipitate crystallizes quickly. Many of the crystals are spherical and others are rosettes of plates (10).

SODIUM PHOSPHATE.—Small rods formed in the 1:1000 solution on stirring. In the 1:200 solution cubical or six-sided forms predominate. In the 1:50 solution there are many sharp, clear-cut crystals formed at once. They are normally long needles. Limit of reaction is about 1:2000, but at this dilution the crystals are not characteristic.

AMMONIUM THIOCYANATE.—Small rods are formed on stirring the 1:1000 solution and a very dense mass of



crystals appear in the more concentrated solution (Plate XXV, Fig. 6) (2) (3) (8).

**CHROMIC ACID.**—Crystals are quickly formed in solutions from the amorphous precipitates which are thrown down in all but the 1:1000 solution. They are two kinds, the most common being rectangular, having lines joining the opposite corners. They do not polarize. The other crystalline form is branching and does not polarize. At the 1:200 dilution the last is the most common form of crystals. A few small crystals are formed in 1:5000 solution. The reaction of potassium dichromate is similar to the above and was described by Wormley (Plate XXIII, Fig. 2) (8) (1).

**POTASSIUM CHROMATE.**—Rods sometimes in rosette form are formed in solutions up to 1:500 (3) (10).

**GOLD CHLORIDE.**—A dense, amorphous precipitate is thrown down upon adding the reagent. This crystallizes out rapidly. The crystals are dense rosettes. They are light-brown in color and do not polarize brilliantly.

These crystals grow to a large size even in a 1:10 solution. The weight of the cover glass is sufficient to break the crystals.

The 1:50 solution is too concentrated for satisfactory results, as crystals are formed in a dense mass.

Some fairly large and characteristic crystals are formed at a dilution of 1:20,000 (Plate III, Fig. 4) (1) (8) (10).

**PLATINUM CHLORIDE.**—Clear-cut crystals are quickly formed from the amorphous precipitate in all the solutions. There is considerable variation in their appearance, though all are of the same general type. The rosette clusters formed break down and assume in many instances the

form shown in plate after three to five minutes. In a 1: 15,000 solution great numbers of very small crystals are formed, but they are not characteristic (Plate V, Fig. 4) (1) (8) (10) (18).

The above test, using dichloride of platinum, was described by Wormley (4).

**PALLADOUS CHLORIDE.**—The crystals are large rosettes, the arms having a much curved and irregular shape. There are also a number of very small crystals which float at the surface of the drop. A few small crystals are formed in a 1: 12,000 solution. Wormley states that these crystals are similar to those formed with platinum chloride (Plate VII, Fig. 3) (1) (3).

**MERCURIC CHLORIDE.**—The crystals are fairly large and gracefully curved in the 1: 1000 solution. They polarize but slightly. In the more concentrated solutions they are dense rosettes. A few crystals are formed in a 1: 3000 solution (Plate IX, Fig. 5) (4) (8).

**FERRIC CHLORIDE.**—Crystals are formed slowly in the 1: 200 solution. They are small and spherical. In the 1: 50 solution a dense mass of large needles are formed at once. There are also great numbers of small, spherical crystals formed. The test is not sensitive.

**ZINC CHLORIDE.**—Good-sized, sheaf-like crystals are formed quickly in the 1: 200 solution. They polarize brilliantly. Needles are formed but slowly in the more dilute solutions unless the solution be stirred.

**ZINC-CHLOR-IODIDE.**—Great numbers of small, dark crystals are formed in the 1: 1000 solution. There are two forms of crystals in the 1: 200 solution, one like that formed with zinc chloride and the other spherical in appearance, which does not polarize. In the 1: 50 solution these crys-

tals are fine rosettes. The limit of reaction is 1:10,000 (Plate XXVII, Figs. 4 and 5).

**WAGNER'S REAGENT.**—Dense precipitates appear in all the solutions. There are two forms of crystals, one is light in color and appears to float at the surface; the other appears as large needles or rods in masses in the more concentrated solutions. The crystals formed in a 1:2000 solution are small and not characteristic (1).

Kraut's reagent gives reaction like above.

**POTASSIUM IODIDE.**—No amorphous precipitates are formed. Needle-shaped crystals, often in rosettes, are formed in the more dilute solutions, and these must be stirred for quick results.

Dense rosettes of plates are formed in the 1:50 solution (1).

**MARME'S REAGENT.**—In the 1:1000 solution we have first an amorphous precipitate which is not very dense, and from this small, silvery-looking masses, possibly crystals, are formed rather slowly.

We also have a crystal formation when the solution stands for a short time. These crystals are quite different from the other forms and are sharp-cut rosettes of small plates. They polarize brilliantly.

A 1:25,000 solution gives a few small crystals, but they are not at all characteristic. The 1:1000 crystals are quite normal in appearance (Plate XVII, Fig. 6).

**MAYER'S REAGENT.**—A dense, amorphous precipitate and two forms of crystals are formed. The first form of crystals floats on the surface. They are light in color, do not polarize, and are not clear-cut. The other form is darker, polarizes slightly and forms more slowly than the first. They are rosettes of needles or rods in the more con-

centrated solutions. A good number of small crystals was formed in a 1: 20,000 solution (Plate XVI, Figs. 4 and 5) (1) (10).

**POTASSIUM FERRICYANIDE.**—Rosettes of rods or plates appeared in the two more concentrated solutions only (10) (15).

Potassium ferrocyanide forms crystals similar to above, but the reaction is more sensitive (8) (10).

**POTASSIUM CYANIDE.**—Great numbers of rods often in rosettes formed in all the solutions. A few small crystals were formed in a 1: 3000 solution. Stir the solutions for quick results.

**PHOSPHOMOLYBDIC ACID.**—Crystals formed only in the 1: 50 solution. They are large rods of dense masses and much of the heavy, amorphous precipitate does not crystallize.

Sodium phosphomolybdate gives results like the above.

**SACCHARIN.**—A few small crystals are formed on stirring a 1: 200 solution. A very dense, amorphous precipitate is formed in the 1: 50 solution. This turns into oil-like drops which soon crystallize into plates in rosettes. They are formed slowly unless the solution be stirred.

**PICRIC ACID.**—The crystals are large, green rosettes gracefully curved and are formed in all the solutions from the amorphous precipitates. Crystals are formed on stirring a 1: 10,000 solution (Plate XX, Fig. 1) (1) (6) (10) (11) (12).

**MILLON'S REAGENT.**—Rosettes of needles appear in the 1: 50 solution only. A few small crystals normally six-sided are sometimes formed in the 1: 500 solution.

The following color reaction was noted. Ammonium vanadate produced a pink coloration in all the solutions.

## THEBAINE

Four crystalline and twenty-six non-crystalline precipitates were obtained.

POTASSIUM HYDROXIDE.—Great numbers of small rods are formed in the 1: 1000 solution. They polarize brightly.

In the more concentrated solutions the crystals are rosettes of plates or rods formed from the amorphous precipitate.

The same crystal forms as above are given with sodium carbonate or potassium cyanide (Plate XVI, Fig. 2) (8).

PLATINUM CHLORIDE.—The best crystals are obtained by using a very small amount of this reagent and in the 1: 50 solution only. They are fine needles in rosettes or sheaves. In more dilute solutions crystallization is poor and the crystals are small and spherical (10).

## THEOBROMINE

No satisfactory microchemical tests were obtained.

Not being soluble in water or in dilute hydrochloric acid, a dilute solution in 10 per cent. potassium hydroxide was used, but in order to obtain the following crystals the drop of the solution must be allowed to dry down and thus become more concentrated before applying the reagent.

GOLD CHLORIDE.—A dense mass of light-green, needle-like crystals are formed.

KRAUT'S REAGENT.—A dense mass of dark, reddish-brown needles or small plates is formed. Sometimes the crystals are small and spherical. A pink color is developed around the edge of the drop.

PICRIC ACID.—With alcoholic solution rod crystals are formed at once on stirring all solutions. No amorphous precipitates formed.

## TROPACOCAINE HYDROCHLORIDE

Twenty crystalline and only four non-crystalline precipitates were obtained.

CHROMIC ACID.—The limit of reaction is about 1: 2000. At this dilution a few small crystals are formed on stirring.

Small, diamond-shaped crystals are formed on stirring the 1: 1000 solution. They are very brilliant under polarized light. The two more concentrated solutions give beautiful large rosettes of plate-like forms. Amorphous precipitate formed in the 1: 50 solution only (Plate XXIII, Fig. 3).

GOLD CHLORIDE.—This is a very sensitive test, as a considerable number of small crystals are formed in a 1: 30,000 solution on stirring. Crystals form at once in the 1: 1000 solution. They are fairly large and clear-cut. A few crystals float at the top of the drop. They all have a rather rough-appearing surface. The crystals are of the same general form, but they are much larger when the drop is not stirred. The more concentrated solutions form dense masses of crystals at once from the amorphous precipitate (Plate III, Fig. 5) (15).

PLATINUM CHLORIDE.—This is a sensitive test. Beautiful large crystals are formed in the more dilute solutions. These crystals normally have cross-arms forming an acute angle one with another. The crystals are produced in such masses that their form is not perfect in more concentrated solutions. A few very small crystals are formed in a 1: 20,000 solution (Plate V, Fig. 5) (15).

PALLADOUS CHLORIDE.—This is another sensitive test for tropacocaine. Crystals formed in all the solutions vary in shape. Normal crystals have a very short cross-arm at

an acute angle to the main axis. Solutions of 1:100 and under are too concentrated for best results. Numbers of small crystals are formed in a 1:4000 solution (Plate VII, Fig. 4).

**MERCURIC CHLORIDE.**—Small, jagged crystals are formed on stirring a 1:5000 solution. Solutions under 1:100 are too concentrated and over 1:1000 too dilute for satisfactory crystal formation. In the 1:200 solution the crystals are normally very large and jagged plates in rosettes (5).

**FERRIC CHLORIDE.**—Crystals appear in the two more concentrated solutions only. In a 1:100 solution an amorphous precipitate is formed which is at once redissolved, but by adding sufficient of the reagent the precipitate finally does not dissolve but crystallizes out in moss-like forms. The crystals are of the same general type, but somewhat smaller on stirring the solution.

**ZINC CHLORIDE.**—Crystals are formed in the more concentrated solutions only. They are rods or are diamond-shaped and formed in great numbers on stirring; 1:200 is about the limit of reaction.

**ZINC-CHLOR-IODIDE.**—This test is sensitive, crystals being formed in a 1:5000 solution. The crystals are similar to those formed with zinc chloride (Plate XXVII, Fig. 6).

**WAGNER'S REAGENT.**—This is another sensitive test for this alkaloid.

In the 1:1000 solution, an amorphous precipitate is formed which settles down upon the slide and after a time beautiful, clear-cut crystals of a light-yellow color are formed. They do not form rapidly in all cases and vary considerably in shape. In the 1:500 solution the crystals

which form first float on top of the drop, then darker crystals form which are usually a cluster of needles; 1: 50 is too concentrated for the best results. Great numbers of crystals are formed in a 1: 5000 solution.

Kraut's reagent gives results like the above (Plate XIII, Fig. 5).

POTASSIUM IODIDE.—Many plates are formed in all the solutions, but they are small in the 1: 1000 solution and form slowly on stirring.

MARME'S REAGENT.—The crystals are moss-like in appearance. The test is sensitive, crystals being formed on stirring a 1: 20,000 solution. In the 1: 1000 solution the dense, amorphous precipitate forms crystals slowly unless the drop be stirred (Plate XVIII, Fig. 1).

MAYER'S REAGENT.—On stirring the 1: 1000 solution, small crystals are formed in great numbers. They are of two kinds, the lighter colored ones float on the surface; the others are dark and appear as in the photograph. The limit of reaction is about 1: 20,000 (Plate XVI, Fig. 6).

POTASSIUM FERRICYANIDE.—The limit of reaction is about 1: 200. Large plates are formed from the amorphous precipitate in this solution, but not quickly unless stirred. These crystals are very brilliant under polarized light.

POTASSIUM FERROCYANIDE.—Crystals are formed only in the concentrated solutions. They are normally clear-cut rods or plates and polarize brilliantly.

POTASSIUM PERMANGANATE.—Crystals are formed quickly from the amorphous precipitate in the 1: 1000 solution. They are purple in color and appear to be made up of a number of thin plates one upon the other (Plate XXIII, Fig. 6) (15). The crystals normally have a very



graceful, wing-like appearance. The crystals that are formed when the solution is stirred are usually rectangular in form, often with a V-shaped recess in either or both ends; 1:4000 appears to be near the limit of reaction.

**PICRIC ACID.**—Crystals are quickly formed from the amorphous precipitate in the 1:1000 solution. They are normally rosettes, but variations from the normal form occur according to the amount of reagent used. The weight of the cover-glass is sufficient to break the crystals. Crystals in the two more concentrated solutions form more slowly. A few small crystals are formed in a 1:8000 solution. With an alcoholic solution of this reagent a few small needles are formed in a 1:20,000 solution (Plate XX, Fig. 2) (15).

**MILLON'S REAGENT.**—A dense, crystalline precipitate is formed in a 1:50 solution. They show many colors and polarize brightly. Blade-like rosettes are the normal forms. No crystals or precipitates form in the more dilute solutions.

**SODIUM NITRO-PRUSSIDE.**—No reaction in the more dilute solutions. Large crystals are formed in a 1:100 solution. These crystals have a very rough-appearing surface and many fine needles projecting from this give the crystals a cactus-like appearance.

**AMMONIUM THIOCYANATE.**—The slight, amorphous precipitate in the 1:50 solution crystallizes on stirring at once into fine plates often in rosettes.

Twenty different tests for tropacocaine were tried on a mixture of this alkaloid and some other alkaloid in equal amounts. In this way forty different alkaloids were tested with tropacocaine. This makes a total of eight hundred tests. The results obtained were as follows: The test for

tropacocaine was not affected in 450, or 56 per cent., of the cases; was slightly affected in 84, or 15 per cent., and was spoiled in 266, or 29 per cent., of the total tests made.

Some reactions are not affected by the presence of another alkaloid and others are very easily spoiled. If both alkaloids in a mixture precipitate with the reagent used, the test is most likely to be spoiled.

It appears that often the amount of reagent used has more effect on the shape of the crystal than the presence of another alkaloid.

#### YOHIMBINE HYDROCHLORIDE

One crystalline precipitate only and twenty-eight amorphous precipitates were obtained.

POTASSIUM CYANIDE.—Rosettes of crystals of good size are formed from the amorphous precipitates, but they form very slowly and in the 1:200 solution only. They show distinct polarization crosses (Plate XXI, Fig. 3).

The following color reactions were noted:

Froehde's reagent gives a deep-blue color in the 1:200 solution which, on standing, changes to green.

Millon's reagent gives a yellow color on standing.

## CHEMICAL EXAMINATIONS

### DIVISION OF DRUGS

The following tests and observations bearing upon the question of the authenticity and purity of the alkaloids used in this work were made. The authorities cited are:

ALLEN: "Commercial Organic Analysis" (fourth edition), 1909-14.

BRÜHL, HJELT and ASCHAN: "Die Pflanzen-Alkaloide," 1900.

HENRY: "The Plant Alkaloids," 1913.

PICTET-BIDDLE: "Vegetable Alkaloids," 1904.

ROSENTHALER: "Der Nachweis Organischer Verbindungen," 1914.

SCHMIDT: "Pharmaceutische Chemie" (fifth edition), 1911.

"United States Pharmacopœia" (eighth edition, revised), 1905.

WINTERSTEIN AND TRIER: "Die Alkaloide," 1910.

Reference is made to these works for the details of pharmacopœial tests and other well-known tests and reagents. It may be mentioned, however, that by Mecke's (Lafon's) reagent is understood a 0.5 per cent. solution of selenious acid in sulphuric acid.

The centigrade thermometer was used in reading all temperatures.

Aconitine, potent. Merck, crystals.

Crystalline powder presenting some rhomboidal and prismatic fragments.

M.P., 190°, heated rapidly to 185°, then 1° per minute.

(U.S.P. states M.P.  $195^{\circ}$  if rapidly heated, but  $182^{\circ}$  with decomposition if slowly heated. Henry,  $197-8^{\circ}$ . Winterstein and Trier,  $197-8^{\circ}$ . Pictet quotes Dunstan,  $189-190^{\circ}$  and Freund and Beck,  $197-8^{\circ}$ ; Brühl, when rapidly heated,  $197-8^{\circ}$ ; Rosenthaler,  $197-8^{\circ}$ ; Schmidt quotes Ehrenberg and Purfurst,  $194^{\circ}$ .)

With sulphuric acid and ammonium vanadate gave an orange color. On warming with sulphuric acid the solution was at first colorless, carbonizing on prolonged heating.

Gave no Vitali reaction.

Was dextrorotatory; the hydrochloride was levorotatory.

The 1:1000 solution of the sulphate gave with N/10 potassium permanganate a precipitate barely perceptible under the microscope.

Anhalonine Hydrochloride, Merck.

M.P.  $181-2^{\circ}$ .

(Schmidt,  $254-5^{\circ}$ .)

The nearly colorless solution in sulphuric acid did not become colored on warming.

Sulphuric acid with a trace of nitric acid produced a violet-red color fading to brown.

Nitric acid produced a reddish-purple color fading out and not becoming blood-red, as stated by Schmidt.

Apocodeine Hydrochloride, Merck.

M. between  $150^{\circ}$  and  $160^{\circ}$ ; not sharp.

(Schmidt states that its properties are similar to those of apomorphine.)

Its solution did not turn blue or black with ferrous sulphate solution.

Upon shaking its acetic acid solution with potassium

86 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

iodate and ether and diluting with water, the ether formed a greenish layer.

On adding 10 per cent. solution of ferric chloride to the water solution it turned brown.

The substance with Marquis' reagent produced no color; Mecke's reagent produced a dirty-green color turning black; Froehde's reagent produced a dark-blue, becoming greenish-black.

Apomorphine Hydrochloride, Merck, Crystals.

M. 205–210°, decomposing with a dark color.

(U.S.P. decomposes between 200° and 210°.)

U.S.P. tests:

When shaken with 100 parts of water, the latter acquired no green color.

Conformed to the color tests of the U.S.P. except that with sulphuric acid and paraldehyde, the color was greenish-yellow rather than green. Also, dilute ferric chloride solution gave not a red color, but violet, changing to purple. Ferric chloride, T.S. U.S.P.8, gave first a purple and, as more was added, a deep-red color.

Arecoline Hydrobromide, Merck.

M.P., 168–170°.

(Henry, 167–8°. Crystallized from alcohol. Schmidt, 167–8°; crystallized from alcohol. Brühl, 167–8°; crystallized from alcohol. Rosenthaler, 170°.)

Water solution gave no precipitate with tannic acid.

Aspidospermine, Merck.

Crystals according to Fraude.

M.P., 205–6°.

(Schmidt, 205–6°; Pictet, 205–6°; Henry, 205–6°; Brühl, 205–6°; Winterstein, 205–6°; Rosenthaler, 205–6°.)

The solution in dilute sulphuric acid being boiled with

a small amount of potassium chlorate assumed a fuchsin red color. On evaporating with platinic chloride and hydrochloric acid, a violet-purple residue was left. On triturating with sulphuric acid and a little lead peroxide, the mixture turned brown, then red.

Atropine Sulphate, Merck.

M.P., 189–190°. Dried first at 120°, then over sulphuric acid.

(U.S.P., M.P., about 189.9°. If free from hyoscyamine about 188°. Henry, about 189.9°. Schmidt, about 183°. Rosenthaler, about 180° dry.)

U.S.P. tests:

Gave Vitali's reaction. The solution in water gave no precipitate with either platinic chloride or gold chloride, but when the alkaloid was extracted and converted into the hydrochloride, its solution gave no precipitate with platinic chloride, but a copious one with gold chloride.

The chloraurate melted at 137°.

Benzoyl Ecgonine, Merck.

Crystals appeared efflorescent.

M.P., not sharp, about 175°. After drying, M.P., 191–2°, fairly sharp.

(Schmidt, 86–7°; anhydrous, 195°; Henry, 86°; anhydrous, 195°; Brühl, 86–7°; anhydrous, 195°; Pictet, 92°; anhydrous, 195°; Winterstein, anhydrous, 195°.)

Chloraurate, air-dry, melted 207–8°.

Berberine, Kahlbaum.

Gradually darkened above 150° to black, melting above 200°.

(Schmidt about 140°; Brühl, 145°, decomposing above 150°. Winterstein, about 150°, dry. Henry, M.P., indefinite, decomposing above 110°, liquid only at 160° with

88 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

decomposition. Pictet, melts at  $120^{\circ}$ , anhydrous. Rosenthaler states that the base known in the solid form is not berberine (hydroxide) but berberinal, M.P.,  $144^{\circ}$ .)

Water solution neutral to litmus.

Formed with sulphuric acid a yellow solution becoming olive-green, then brown.

Formed with nitric acid an orange solution immediately becoming brown.

Upon adding bromine water drop by drop to the water solution of the alkaloid the precipitate first formed dissolved, on shaking, to a reddish-brown solution; further addition of bromine water produced a brown precipitate, dissolving on warming to a red solution.

The acetic and sulphuric acid solution of the alkaloid on treatment with zinc was nearly decolorized. On making this solution alkaline with ammonia and shaking out with ether or chloroform the evaporation residue was brownish-yellow, amorphous, and partly soluble in water.

Betaine Hydrochloride, Merck.

M.P., about  $235-6^{\circ}$  with decomposition.

(Schmidt, with decomposition,  $213-15^{\circ}$ ; Rosenthaler, with decomposition,  $227-8^{\circ}$ .)

The chloraurate, recrystallized with hot water, began to soften about  $190^{\circ}$ , melted entirely with sudden evolution of gas at  $245-8^{\circ}$ .

(Schmidt, vol. ii, Part I, p. 450 [1910], states that the chloraurate recrystallized from hot 1 per cent. hydrochloric acid, melts at  $248^{\circ}$ , from hot water,  $209^{\circ}$ .)

Brucine, Merck, Reagent.

Softened at  $173^{\circ}$ . M.P.,  $176-7^{\circ}$ . Dried at  $110^{\circ}$ .

(Henry, M.P., anhydrous,  $178^{\circ}$ ; Pictet, M.P., anhydrous,  $178^{\circ}$ ; Schmidt, M.P., anhydrous,  $178^{\circ}$ ; Brühl, M.P., anhydrous,  $178^{\circ}$ ; Rosenthaler, M.P., anhydrous,  $178^{\circ}$ .)

With nitric acid a blood-red color was produced gradually fading to yellow. On adding stannous chloride it became purple.

Caffeine.

M.P., 231–2°.

(U.S.P., sublimes about 178°; dried at 100° to constant weight, melts at 236–8°. Schmidt, begins to sublime a little about 100°, melts at 230–5°. Winterstein, sublimes at 221°, melts dry at 234°. Henry, sublimes at 176°, melts dry at 234–5°. Pictet, melts dry 234–5°. Rosenthaler, melts dry 234–5°.)

Dissolved in sulphuric acid and in nitric acid without production of any color.

Murexide test positive.

Sulphuric acid with potassium dichromate produced a yellowish-green color, becoming green.

Its solution was not precipitated by Mayer's reagent.

Calycanthine Sulphate.

M.P., 223–4°.

The substance with nitric acid gave a green color. Sulphovanadic acid gave a blood-red color. Sulphuric acid containing a little potassium dichromate gave a blood-red color, finally becoming greenish. Froehde's reagent gave a yellow color, finally becoming red.

Chelidonine, Merck.

M.P., 145–150°, not sharp.

(Henry, 135–6°. Pictet, 135–6°. Schmidt, 136°. Winterstein, 136°. Rosenthaler, 135–6°.)

The solution in warm alcohol, slightly acidified with HCl, was precipitated with gold chloride. Brown precipitate of microscopic prisms or needles. M.P., 192–3°.



## 90 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Sulphuric acid turned the powder black and the liquid finally became faint violet.

Sulphuric acid with a trace of nitric acid gave a brown color fading to yellow. The mixture with sugar and water, to which, after a few minutes, sulphuric acid was added, turned purplish-brown.

Froehde's reagent gave a dirty-green color, becoming grass-green, then dirty-green. Sulphovanadic acid gave a light-green color, becoming dark-green, then dirty-green.

Cinchonidine Sulphate, Bullock and Crenshaw.

M.P., 205–6°.

(U.S.P., loses water of crystallization at 100°, darkens at 203°, melts 205.3°.)

U.S.P. tests:

The 1:1000 solution in dilute sulphuric acid was very slightly fluorescent. The substance treated with sulphuric acid gave no color; on adding potassium chromate turned yellowish-green, then green.

On treating 0.5 gram with water and Rochelle salt and filtering, the filtrate gave no precipitate with one drop of ammonia water. (No excess of cinchonine or quinidine sulphate.)

The aqueous solution was slightly alkaline to litmus, laevorotatory. In the solution barium chloride produced a precipitate insoluble in hydrochloric acid.

The base precipitated by ammonia was only slightly soluble in ammonia, but quite so in ether.

Cinchonine Sulphate, Feidt.

M.P., 198–9°.

U.S.P.—M.P., 198.5°.

The 1:1000 aqueous solution was slightly alkaline to litmus, dextrorotatory, not perceptibly fluorescent, but be-

came so on addition of a few drops of sulphuric acid. The aqueous solution with barium chloride gave a white precipitate insoluble in hydrochloric acid. The substance was nearly soluble in 80 parts of chloroform and was not discolored by sulphuric acid.

Cocaine Hydrochloride.

M.P., 188–9°. (U.S.P., about 189.9°; Brühl, 181.5°; when quite pure, 201–2°; Henry, 186°; Rosenthaler, 183°; Schmidt, 186°, anhydrous.)

U.S.P. tests:

The aqueous solution gave with silver nitrate white precipitate insoluble in nitric acid.

On applying the U.S.P. test for excess of isotropyl cocaine, a crystalline precipitate was obtained, the supernatant liquid not appearing opalescent, but still not perfectly clear, owing to some precipitate remaining in suspension.

On applying the test with potassium permanganate, the color did not fade in one-half hour.

On heating with sulphuric acid, vapors of benzoic acid escaped.

Codeine Sulphate Crystals, U.S.P., Mallinckrodt.

Began to turn brown about 215–220°. M.P., 277°.

(U.S.P., loses water of crystallization at 100°, decomposes above 200°, residue melts 278°; Henry, M.P., 278° dec.)

U.S.P. tests:

The aqueous solution was neutral to litmus; with barium chloride formed a white precipitate insoluble in HCl.

With potassium ferricyanide and ferric chloride no blue color appeared at once.

On adding to the substance sulphuric acid, no color

## 92 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

appeared in the cold, on warming the solution became violet, and on further adding nitric acid, red.

Mecke's reagent produced a green color, turning blue and then green. Marquis' reagent produced a violet color, turning blue.

Colchicine.

Dried over sulphuric acid, no sharp M.P. Softened at  $135^{\circ}$ , but was not in clear fusion at  $160^{\circ}$ .

(U.S.P., dried over sulphuric acid, M.P.,  $142.5^{\circ}$ ; Winterstein, no sharp M.P.,  $143-7^{\circ}$ ; Pictet,  $145^{\circ}$ ; Schmidt,  $145^{\circ}$ ; Brühl, quite dry,  $143-7^{\circ}$ ; Henry, dry,  $143-7^{\circ}$ ; Rosenthaler, about  $145^{\circ}$ .)

U.S.P. tests:

The aqueous solution was yellow, neutral to litmus and lævorotatory. The substance with sulphuric acid gave a yellow solution which nitric acid turned greenish-blue, then red, then yellow. On adding excess of potassium hydroxide it became red.

The substance on boiling with hydrochloric acid and ferric chloride formed a yellow solution, becoming green, which imparted a reddish color to chloroform when shaken with same.

Coniine, Merck, Pure.

Light-brown, mobile liquid.

Dextrorotatory in alcoholic solution. Turned litmus paper blue, leaving no fatty stain.

To the alcoholic solution a little carbon bisulphide was added and the mixture was warmed. In one portion of this, copper sulphate 0.1 to 0.2 per cent. solution produced a brown precipitate, soluble in ether; in another portion ferric chloride solution produced a brown color soluble in ether; in another, uranium nitrate solution produced a red color soluble in toluene.

A water solution of the hydrochloride on evaporation left a residue of rush-like crystals.

On adding to a solution of the same sodium hydroxide solution and distilling with steam, an alkaline distillate, with an odor of coniine, was obtained.

Corydaline Alkaloid, Merck.

M.P., 127°.

(Schmidt, 134-5°; Pictet, Brühl, 134-5°; Winterstein, 134-5°; Henry, 135°.)

The alcohol solution was dextrorotatory.

Froehde's reagent gave a dark-blue color, becoming dirty-green. Sulphovanadic acid gave a blue color, becoming bluish-gray.

Cytisine Hydrochloride, Merck.

M.P. not below 280°.

The aqueous solution was laevorotatory.

On making the solution alkaline with ammonia, shaking out with chloroform and evaporating the chloroform in several portions, the residue on adding ferric chloride turned brown, becoming a dirty-blue on adding a few drops of hydrogen peroxide. On warming on the water bath this became yellow.

On warming another portion of the residue with 2 c.c. nitric acid, it turned yellow, and on dilution with water no precipitate appeared.

Daturine Sulphate, Merck.

Dried at 100°, M.P. 200°; dried at 120°, M.P. 204-5°.

(Henry states that the alkaloid from stramonium fruits is identical with atropine; likewise Schmidt and Winterstein. Brühl states that the identity, though questioned, is now admitted.)

Gave Vitali's reaction. The aqueous solution was

#### 94 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

lævorotatory. The solution with barium chloride gave a white precipitate insoluble in hydrochloric acid. The properties indicate that this is hyoscyamine sulphate rather than atropine sulphate.

Dionine, Merck.

M.P., 123–5°. (Henry, M.P., 123–5°; Rosenthaler, begins to melt 110°, transparent 120°.)

Gave Pellagri's reaction.

With Froehde's reagent, yellowish-green color, becoming blue. Marquis' reagent, bluish-purple.

The aqueous solution upon addition of silver nitrate gave a white precipitate, insoluble in nitric acid.

Ecgonine Acid Hydrochloride, Rhombs.

M.P., 245–250°.

Henry, Ecgonine hydrochloride, rhombs, 246°; (d) Ecgonine hydrochloride, rhombs, monoclinic prisms, 236°; (dl) Ecgonine hydrochloride, rhombs, slender needles; dry, 149° with dec.; Brühl, rhombic tables, 246°; (d) Ecgonine hydrochloride, rhombs, 236°.)

A portion was dissolved in a minimum amount of water, platinic chloride added and then absolute alcohol and allowed to stand. The scanty precipitate was washed three times by decantation with absolute alcohol and dried at 140–145°, and then over sulphuric acid in a desiccator for several days. M.P., 209–210°.

Allen, "Commercial Organic Analysis," 1912, 6, 338, states that  $B_2H_2PtCl_6$  melts at 226°.

Heroine (Diacetylmorphine Hydrochloride) Mallinckrodt.

M.P., 225–6°. (See Schmidt 2, Part 2, 1716.) The substance with Froehde's reagent gave a purple color; with Marquis' reagent a purple color; with Mecke's re-

agent a green color like morphine; with nitric acid a yellow color turning green.

On warming with sulphuric acid and alcohol the odor of ethyl acetate was perceptible.

The aqueous solution with ferric chloride gave no blue color; with silver nitrate a white precipitate insoluble in nitric acid; barium chloride, no precipitate.

Homatropine Hydrobromide, Powers-Weightman-Rosengarten.

M.P., 209–210°. A sample of Mallinckrodt's, M.P., 208–9°. (U.S.P., 213–8°; Henry, 213.8°.)

U.S.P. tests:

The aqueous solution was neutral to litmus; not precipitated by tannic acid or platinic chloride. In it iodine solution produced a brown precipitate, silver nitrate a white precipitate, insoluble in nitric acid. On adding to it chlorine water and shaking with chloroform, the latter was colored brown by free bromine.

The substance gave no Vitali reaction. On treating it with sulphuric acid containing a trace of potassium dichromate a transient pink color appeared which was slowly replaced by green.

On making the aqueous solution alkaline with potassium hydroxide, shaking out with ether and evaporating the latter, the residue was not crystalline, but rather semi-liquid and sticky. No M.P. of the free alkaloid was obtainable.

The alkaloid turned yellow and then red on warming with mercuric chloride solution, as stated by U.S.P.

Hydrastine Merck-Alkaloid-Highest Purity.

M.P., 131°. (U.S.P., 131°; Winterstein, 132°;

96 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Pictet, 132°; Brühl, 132°; Schmidt, 132°; Henry, 132°; Rosenthaler, 132°.)

U.S.P. tests:

Alkaline to litmus. The chloroform solution was lævotatory. Sulphuric acid produced a yellow color, becoming purple on heating. Froehde's reagent produced a green color, changing to brown; nitric acid produced a reddish-yellow color; Mecke's reagent produced a red, changing to brown; sulphuric acid with potassium dichromate, a red color changing to brown.

The sulphuric acid solution on addition of potassium permanganate acquired a blue fluorescence.

Hydrastinine Hydrochloride, Merck.

M.P., not sharp; softens about 193°; M.P., about 198°.  
(Schmidt, 212°; Henry, 212°; Rosenthaler, 210°.)

U.S.P. tests:

The aqueous solution gave a blue fluorescence and was slightly alkaline to litmus; with bromine water gave a yellow precipitate soluble in ammonia.

Potassium dichromate solution produced a precipitate soluble on heating and crystallizing out again on cooling.

Ammonia water produced no precipitate.

Sodium hydroxide produced a transient turbidity followed by a precipitate on standing.

The substance with sulphuric acid gave only a faint-yellow color; with nitric acid a yellowish color; with sulphuric and nitric acids a red color.

Sulphuric acid and ammonium vanadate produced an orange color turning a dark-brown and then fading.

Hyoscyne (see Scopolamine).

Hyoscyamine Hydrobromide, Merck—from Belladonna-Cryst.

M.P., 147–8°. (U.S.P., 151.8°; Henry, 151.8°.)

U.S.P. tests:

The chloraurate melted 159–160°. The aqueous solution was neutral to litmus, lævorotatory; with silver nitrate gave a precipitate insoluble in nitric acid, soluble in ammonia; with platinic chloride, no precipitate.

The solid substance gave Vitali's reaction; with sulphuric acid no color was produced, and the further addition of nitric acid produced no color.

Morphine Alkaloid.

M.P., 253–4°. (U.S.P., when rapidly heated, 254°; Brühl, with decomposition, about 230°; Schmidt, cautiously heated, about 230°, without decomposition; above 230° or upon rapid heating it decomposes; Pictet, about 247° with decomposition; Henry, 254°, with decomposition; Rosenthaler, 230°.)

U.S.P. tests:

The aqueous solution was alkaline to litmus; Mayer's reagent gave a gelatinous precipitate; sodium phosphomolybdate gave a yellow precipitate forming a blue solution upon addition of ammonia.

Upon warming with solutions of ferric chloride and potassium ferricyanide, it turned blue. The neutral solution gave a blue color with ferric chloride and the acidified solution gave no color.

Solid substance: with sulphuric acid, cold, gave no color, but on heating a brownish-purple. With sulphuric acid and potassium iodate dark-brown color; with Mecke's reagent, blue color becoming green and then brown; with Froehde's reagent, reddish-purple color becoming blue; with Marquis' reagent, purple color; with sulphuric acid



98 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

and potassium dichromate, colorless, then green; with nitric acid, orange color becoming yellow.

Narceine, Eimer and Amend.

M.P., 165–6°; dried at 105–110°, began to melt at 165–6°; not entirely melted at 220°. (Henry, 170°, or 140–145° dry; Pictet, 170–1°, or 145° dry; Schmidt, 162–5° air-dry; Brühl, 170°, dry at 100°, melts 140–5°; Winterstein, with 3 H<sub>2</sub>O melts 170°, anhydrous 140–5°; Rosenthaler, 170°.)

Substance (see Schmidt, 2, 1742). With Froehde's reagent brown-green color not becoming red; evaporated with dilute sulphuric acid, red color—no violet streaks on adding a trace of nitric acid; with sulphovanadic acid brown color becoming yellow and then pale-reddish; with Marquis' reagent, brown color fading out; with Mecke's reagent, brown to reddish color fading out.

Chlorine water and subsequent addition of ammonia produced an evanescent red color not turning blue upon the addition of iodine solution.

Narcotine, Eimer and Amend.

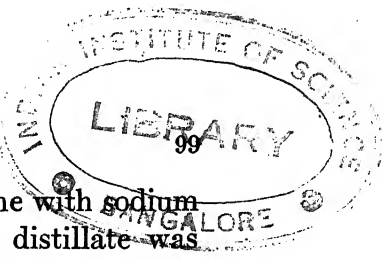
M.P., 172–4°. (Henry, 176°; Pictet, 176°; Schmidt, 176°; Brühl, 176°; Rosenthaler, 176°.)

With Froehde's reagent a green color; with Mecke's reagent, pale-bluish; sulphovanadic acid, red; Marquis' reagent, reddish color becoming yellow; sulphuric acid, yellow color turning red on warming.

Nicotine, Merck, Highest Purity.

A brown liquid apparently somewhat decomposed. The microchemical tests were, however, made on a fresh sample. Turned litmus paper blue and left a fatty-appearing spot. The alcoholic solution was laevorotatory; after acidifying with HCl was dextrorotatory.

## CHEMICAL EXAMINATIONS



The above acid solution was made alkaline with sodium hydroxide and distilled with steam. The distillate was shaken out with chloroform and the latter "blasted off" cold in the presence of dilute HCl. The residue gave precipitates with Meyer's, Kraut's, and Sonnenschein's reagents, and silicotungstic acid. The distillate was alkaline to litmus.

To an ethereal solution of the alkaloid an ether solution of iodine was added and the mixture allowed to stand in a corked tube. Red needles formed but on inspection with reflected light no blue iridescence was apparent. Upon digesting one or two drops of the alkaloid with formaldehyde for some hours and then adding one or two drops of nitric acid a red color was produced. The hydrochloride solution upon evaporation left a non-crystalline residue.

Papaverine, Merck.

M.P., 144–5° (softens 143°). (Winterstein, 147°; Pictet, 147°; Schmidt, 147°; Henry, 147°; Brühl, 147°; Rosenthaler, 147°.)

Substance (Schmidt 2, 1731). With Froehde's reagent gave violet-blue color turning green, then blue, then green; Marquis' reagent, reddish-violet color fading out. Sulphovanadic acid, bluish-green color turning blue; Mecke's reagent a bluish-green color becoming blue and then fading. Chlorine water gave a brownish-gray (not green) solution. Precipitate produced by ammonia had about the same color; no reddish color.

Peronine, Merck.

Melted above 260°. The substance gave Pellagri's reaction.

With Froehde's reagent a bluish-purple color becoming maroon, purplish-gray, then olive, changing rapidly at

## 100 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

first; Marquis' reagent, pink, becoming cherry color; Mecke's reagent, light-green color becoming olive, then greenish-brown; sulphovanadic acid, brownish color; sulphuric acid, cold, produced no color; on warming, a reddish color; addition of a trace of nitric acid turned the solution dark brownish-red.

Physostigmine Sulphate, Merck.

Melting-point, indeterminate; softened about 115°. (U.S.P., M.P., about 140°; softening at 130°; Henry, deliquescent, melts 140°.)

U.S.P. tests:

Aqueous solution faintly acid to litmus. With barium chloride gives a precipitate insoluble in hydrochloric acid. With ammonia an evanescent precipitate which redissolved, the solution turning pink; with gold chloride a purple color and turbidity; with platinic chloride (in concentrated solution only), yellowish precipitate.

The substance with sulphuric acid gave a faint-yellow color; with sulphuric acid and potassium iodate, light-purple to reddish color.

Five mg. treated with nitric acid gave a yellow color, becoming red on warming, and on evaporating the residue became slightly greenish. The latter was not turned violet by fumes of nitric acid; addition of a drop of nitric acid gave a red solution turning greenish on dilution.

Pilocarpidine Nitrate, Harnack-Merck.

M.P., 132° (Schmidt, 136°; Henry, 133°). Applied U.S.P. test for pilocarpine to 10 mg. with hydrogen peroxide, benzol, and potassium dichromate; result negative. Violet color at first, but disappeared on shaking.

Pilocarpine Hydrochloride.

Dried in oven at 103°. M.P., 196-7°. (U.S.P., dried

several hours at  $100^{\circ}$ ; melts  $195.9^{\circ}$ ; Schmidt, about  $200^{\circ}$ ; Brühl,  $200^{\circ}$ ; Rosenthaler, about  $200^{\circ}$ ; Henry,  $204-5^{\circ}$ .)

U.S.P. tests:

Hydrogen peroxide, potassium dichromate and benzol gave a violet color described as characteristic of pilocarpine.

The aqueous solution was faintly acid to litmus and gave a white precipitate with silver nitrate insoluble in dilute nitric acid.

The substance triturated with calomel turned black; on addition of sulphuric acid evolved gas; addition of a particle of potassium dichromate produced a green color.

Piperine, Merck.

M.P.,  $128-130^{\circ}$ .

(U.S.P.,  $130^{\circ}$ ; Henry,  $128-9.5^{\circ}$ ; Pictet,  $128-9^{\circ}$ ; Winterstein,  $128^{\circ}$ ; Brühl,  $128-9.5^{\circ}$ ; Schmidt,  $128-9^{\circ}$ ; Rosenthaler,  $128^{\circ}$ .)

Substance with sulphuric acid produced at first brownish-red color, later becoming greenish; with nitric acid an orange color.

Quinidine Sulphate, Feidt & Co.

M.P.,  $195^{\circ}$ .

Tests (see Schmidt 2, 1787). Warmed 0.5 g. with 10 c.c. of water to  $60^{\circ}$ , added 0.5 g. potassium iodide, stirred and let cool one hour, then filtered. In filtrate one drop 10 per cent. ammonia water produced no precipitate.

Five-tenth gm. and 10 c.c. water acidified with sulphuric acid and 10 c.c. of ether were made alkaline with ammonia and shaken. All the alkaloid was dissolved.

The solution acidified with sulphuric acid was fluorescent; gave the Thalleioquin test. The alcoholic solution of the alkaloid was dextrorotatory.

Quinine Sulphate.

## 102 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Dried at 115–120°.

Melting-point about 218–9° with decomposition. Dried over sulphuric acid, M.P., 209–210° with decomposition. Not sharp. (U.S.P., dried over sulphuric acid, 205°; Schmidt, dried above 150° with decomposition; Henry, dried over sulphuric acid, becomes anhydrous at 115°, melts at 205°.)

U.S.P. tests:

The aqueous solution was neutral to litmus; with barium chloride gave a white precipitate insoluble in hydrochloric acid; gave the Thalleioquin test; when acidified with sulphuric acid gave a blue fluorescence.

The ammonia test for other alkaloid gave a decided turbidity.

The substance with sulphuric acid acquired no color; with nitric acid a faint-yellow color.

Quinoline, Merck, Pure.

Yellow, oily liquid having a slightly alkaline reaction to litmus paper and leaving a fatty stain thereon.

Boiling-point, 236° (determined in a capillary tube containing a Scudder anti-bumping capillary and read on falling temperature at cessation of ebullition). Difficultly soluble in water, readily soluble in alcohol.

Scopolamine Hydrobromide, Merck. True.

M.P., 191°. (Dried two days over sulphuric acid.)

U.S.P., hyosine hydrobromide.

Softens at 100°, melts and loses water of crystallization at 110°. Dried over sulphuric acid, M.P., 191–2°.

(Schmidt, i-scopolamin-hydrobromid dried, 180°; Henry, i-scopolamin-hydrobromid dried, 180°; Brühl, the salt official in Germany dried at 100°, M.P., 187–191°; Rosenthaler, 190–2°.)

The chloraurate, M.P.,  $197^{\circ}$ ; the aqueous solution was neutral to litmus, lævorotatory, silver nitrate produced a precipitate insoluble in nitric acid, but soluble in ammonia.

Chlorine water liberated bromine, imparting a brown color to chloroform. Mayer's reagent with hydrochloric acid gave a precipitate; mercuric chloride, precipitate; phosphotungstic acid, precipitate; picric acid, precipitate; platinum chloride, precipitate.

The substance gave Vitali's reactions.

Solanine, Merck.

Softened at  $250^{\circ}$  with decomposition, not entirely melted at  $270^{\circ}$ . (Henry,  $235^{\circ}$  or  $244^{\circ}$  or  $250^{\circ}$ ; Winterstein,  $262^{\circ}$ ; Pictet,  $235^{\circ}$ ; Brühl,  $244^{\circ}$ ; Schmidt,  $245^{\circ}$ ; Rosenthaler,  $250-260^{\circ}$ .) (See Schmidt 2, 1662.)

The substance with sulphuric acid gave an orange color becoming violet; Froehde's reagent gave a yellow color becoming brown with purple streaks, purple and then greenish; Mecke's reagent gave a brown color, then purple streaks becoming greenish and then brown; sulphovanadic acid, yellow color becoming brown, purple-violet and then olive.

Sparteine Sulphate Crystals, Eimer and Amend.

Dried at  $110^{\circ}$  in oven; melted in its water of crystallization and then solidified; was powdered and dried until no longer coherent; color became slightly yellowish-orange when melted; softened at  $153^{\circ}$ . M.P., not sharp,  $155-7^{\circ}$ .

(U.S.P., loses all water of crystallization at  $110^{\circ}$ , anhydrous, M.P.,  $136^{\circ}$ ; Rosenthaler, Henry and Winterstein give lupinidine as a synonym of sparteine.)

U.S.P. tests:

The aqueous solution was acid to litmus. No precipi-

104 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

tate in any dilution by potassium ferrocyanide 5 per cent. solution.

Barium chloride gave a white precipitate insoluble in HCl. The ether-ammonia-iodine test was positive. The test for volatile alkaloid with potassium hydroxide and litmus paper was positive. The substance treated with sulphuric acid did not carbonize.

Strychnine Hydrochloride, Powers and Weightman.

M.P. not below  $260^{\circ}$ .

The aqueous solution with silver nitrate gave a white precipitate insoluble in nitric acid.

The substance treated with sulphuric acid containing a trace of potassium dichromate gave the characteristic blue-violet color becoming purple, cherry and orange.

Sulphuric acid with ammonium vanadate gave a violet color becoming purple, then cherry.

Sulphuric acid gave no color.

On adding potassium iodate a violet color becoming reddish-purple appeared.

Nitric acid gave no color. On evaporating and treating with ammonia became dark-yellow, and if treated with alcoholic potassium hydroxide solution, orange-red color changing to brown.

Thebaine, Eimer and Amend.

M.P.,  $191-2^{\circ}$ .

(Henry,  $193^{\circ}$ ; Pictet,  $193^{\circ}$ ; Brühl,  $193^{\circ}$ ; Schmidt,  $193^{\circ}$ ; Rosenthaler,  $193^{\circ}$ .)

The substance with sulphuric acid gave a red color; with Froehde's reagent a red color; with sulphovanadic acid a red color.

Theobromine.

M.P. about  $340^{\circ}$ .

(Schmidt and Rosenthaler, sublimes  $290^{\circ}$  without melting; Winterstein, sublimes  $290-5^{\circ}$  without melting; Pictet, sublimes  $290-5^{\circ}$  without melting; enclosed in a tube melts  $329-330^{\circ}$ ; Henry, same as Pictet.)

Substance evaporated with chlorine water and the residue exposed to the fumes of ammonia assumed a purple color (murexide test positive).

Tropacocaine Hydrochloride, Merck.

(Benzoylpseudotropine Hydrochloride.)

M.P. about  $277^{\circ}$  with decomposition.

(Brühl,  $271^{\circ}$ ; Rosenthaler,  $271^{\circ}$ ; Henry,  $283^{\circ}$  with decomposition; Schmidt (see Schmidt 2, 1691).

One-tenth gm. dissolved in 5 c.c. of water and mixed with three drops dilute sulphuric acid and five drops of 1:1000 potassium permanganate solution gave violet color, not diminishing much in one-half hour.

Yohimbine Hydrochloride, Merck (Quebrachine).

M.P. not sharp,  $300-315^{\circ}$  with decomposition.

(Henry,  $295-300^{\circ}$  with decomposition; Brühl,  $287^{\circ}$ ; Rosenthaler,  $285-290^{\circ}$ ; Schmidt 2, 1845, about  $300^{\circ}$ .)

The aqueous solution was made alkaline with ammonia and shaken out with chloroform and the chloroform evaporated. The alkaloidal residue dissolved in sulphuric acid formed a colorless solution. In this particles of potassium dichromate produced grayish streaks not resembling those characteristic of strychnine.

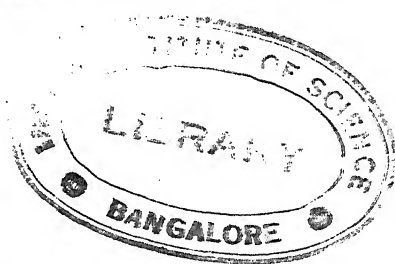
A portion of the alkaloidal residue was warmed in a test-tube with ammoniacal silver nitrate solution. Reduction indicated by formation of a slight mirror.

The substance with sulphovanadic acid gave a blue, turning wine color; with Froehde's reagent slowly developed a blue color turning green.

686







## INDEX TO PLATES

Aconite with Sodium Carbonate .....	Pl. XIII, Fig. 6
Ammonium Thiocyanate .....	Pl. XXV
Anhalonine with Gold Chloride .....	Pl. I, Fig. 1
with Phosphotungstic Acid .....	Pl. XXIV, Fig. 3
with Platinum Chloride .....	Pl. IV, Fig. 1
Apomorphine with Gold Chloride .....	Pl. I, Fig. 2
Arecoline with Kraut's Reagent .....	Pl. XIII, Fig. 1
with Palladous Chloride .....	Pl. VI, Fig. 1
Aspidospermine with Potassium Hydroxide .....	Pl. XV, Fig. 1
with Wagner's Reagent .....	Pl. X, Fig. 1
Atropine with Picric Acid .....	Pl. XIX, Fig. 1
with Wagner's Reagent .....	Pl. X, Figs. 2, 3
Benzoyl-ecgonine with Gold Chloride .....	Pl. I, Fig. 3
Berberine with Hydrochloric Acid .....	Pl. XX, Fig. 5
with Sulphuric Acid .....	Pl. XX, Fig. 6
with Wagner's Reagent .....	Pl. X, Fig. 4
Betaine with Phosphomolybdic Acid .....	Pl. XXIV, Fig. 1
with Phosphotungstic Acid .....	Pl. XXIV, Fig. 4
Brucine with Ammonium Thiocyanate .....	Pl. XXV, Fig. 1
with Chromic Acid .....	Pl. XXII, Fig. 1
with Millon's Reagent .....	Pl. XXVI, Fig. 1
with Palladous Chloride .....	Pl. VI, Fig. 2
with Platinum Chloride .....	Pl. IV, Fig. 2
with Potassium Cyanide .....	Pl. XXI, Fig. 1
with Potassium Hydroxide .....	Pl. XV, Fig. 2
with Potassium Iodide .....	Pl. XVIII, Fig. 2
with Saccharin .....	Pl. V, Fig. 6
with Sodium Nitroprusside .....	Pl. IX, Fig. 6
with Wagner's Reagent .....	Pl. X, Fig. 5
with Zinc Chloride .....	Pl. XXVI, Fig. 5
Caffeine with Gold Chloride .....	Pl. I, Fig. 4
with Kraut's Reagent .....	Pl. XIII, Fig. 2
with Mercuric Chloride .....	Pl. VIII, Fig. 1
Calycanthine with Chromic Acid .....	Pl. XXII, Fig. 2
with Palladous Chloride .....	Pl. VI, Fig. 3
with Platinum Chloride .....	Pl. IV, Fig. 3
Chelidonine with Zinc Chloride .....	Pl. XXVII, Fig. 1
Choline with Phosphomolybdic Acid .....	Pl. XXIV, Fig. 2
Chromic Acid .....	Pls. XXII and XXIII
Cinchonine with Sodium Carbonate .....	Pl. XIV, Figs. 1, 2
Cinchonidine with Platinum Chloride .....	Pl. IV, Fig. 4
with Potassium Hydroxide .....	Pl. XV, Fig. 3
with Sodium Phosphate .....	Pl. VII, Fig. 5
Cocaine with Chromic Acid .....	Pl. XXII, Fig. 3
with Ferric Chloride .....	Pl. III, Fig. 6
with Gold Chloride .....	Pl. I, Figs. 5, 6
with Palladous Chloride .....	Pl. VI, Fig. 4
with Picric Acid .....	Pl. XIX, Fig. 2
with Platinum Chloride .....	Pl. IV, Fig. 5
with Potassium Permanganate .....	Pl. XXIII, Fig. 4

## 108 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Codeine with Ammonium Thiocyanate .....	Pl. XXV, Fig. 2
with Chromic Acid .....	Pl. XXII, Fig. 4
with Marme's Reagent .....	Pl. XVII, Figs. 1, 2, 3
with Millon's Reagent .....	Pl. XXVI, Fig. 2
with Potassium Chromate .....	Pl. XXI, Fig. 4
with Potassium Iodide .....	Pl. XVIII, Fig. 3
with Wagner's Reagent .....	Pl. X, Fig. 6
with Zinc-Chlor-Iodide .....	Pl. XXVII, Figs. 2, 3
Coniine with Marme's Reagent .....	Pl. XVII, Fig. 4
with Phosphotungstic Acid .....	Pl. XXIV, Fig. 5
Corydaline with Mercuric Chloride .....	Pl. VIII, Fig. 2
Cytisine with Gold Chloride .....	Pl. II, Fig. 1
with Mercuric Chloride .....	Pl. VIII, Fig. 3
with Picric Acid .....	Pl. XIX, Fig. 3
with Wagner's Reagent .....	Pl. XI, Fig. 1
Dionine with Mercuric Chloride .....	Pl. VIII, Fig. 4
with Sodium Carbonate .....	Pl. XIV, Fig. 3
with Wagner's Reagent .....	Pl. XI, Fig. 2
Ecgonine with Kraut's Reagent .....	Pl. XIII, Fig. 3
Ferric Chloride .....	Pl. III
Gold Chloride .....	Pls. I, II, III
Heroin with Mercuric Chloride .....	Pl. VIII, Fig. 5
with Picric Acid .....	Pl. XIX, Fig. 4
with Potassium Cyanide .....	Pl. XXI, Fig. 2
Homatropine with Gold Chloride .....	Pl. II, Fig. 2
with Millon's Reagent .....	Pl. XXVI, Fig. 3
with Wagner's Reagent .....	Pl. XI, Figs. 3, 4
Hydrastine with Potassium Hydroxide .....	Pl. XV, Fig. 4
Hydrastinine with Chromic Acid .....	Pl. XXII, Figs. 5, 6
with Palladous Chloride .....	Pl. VI, Fig. 5
with Picric Acid .....	Pl. XIX, Fig. 5
with Platinum Chloride .....	Pl. IV, Fig. 6
with Potassium Permanganate .....	Pl. XIII, Fig. 5
Hydrochloric Acid .....	Pl. XX
Hyoscyamine with Gold Chloride .....	Pl. II, Fig. 3
with Wagner's Reagent .....	Pl. XI, Fig. 5
Kraut's Reagent .....	Pl. XIII
Marme's Reagent .....	Pls. XVII, XVIII
Mayer's Reagent .....	Pl. XVI
Mercuric Chloride .....	Pls. VIII, IX
Millon's Reagent .....	Pl. XXVI
Morphine with Marme's Reagent .....	Pl. XVII, Fig. 5
with Mayer's Reagent .....	Pl. XVI, Fig. 3
with Mercuric Chloride .....	Pl. VIII, Fig. 6
with Potassium Chromate .....	Pl. XXI, Fig. 5
with Potassium Iodide .....	Pl. XVIII, Fig. 4
with Sodium Carbonate .....	Pl. XIV, Fig. 4
with Wagner's Reagent .....	Pl. XI, Fig. 6
Narceine with Gold Chloride .....	Pl. II, Fig. 4
with Palladous Chloride .....	Pl. VI, Fig. 6
with Platinum Chloride .....	Pl. V, Fig. 1
with Potassium Hydroxide .....	Pl. XV, Fig. 6
with Wagner's Reagent .....	Pl. XII, Fig. 1
Narcotine with Potassium Acetate .....	Pl. XII, Fig. 5
with Sodium Carbonate .....	Pl. XIV, Fig. 5

Nicotine with Gold Chloride .....	Pl. II, Fig. 5
with Mercuric Chloride .....	Pl. IX, Fig. 1
Palladous Chloride .....	Pls. VI, VII
Papaverine with Mercuric Chloride .....	Pl. IX, Fig. 2
with Palladous Chloride .....	Pl. VII, Fig. 1
with Potassium Hydroxide .....	Pl. XV, Fig. 5
with Zinc Chloride .....	Pl. XXVI, Fig. 6
Peronine with Potassium Iodide .....	Pl. XVIII, Fig. 5
Phosphomolybdic Acid .....	Pl. XXIV
Phosphotungstic Acid .....	Pl. XXIV
Picric Acid .....	Pls. XIX, XX
Pilocarpidine with Phosphotungstic Acid .....	Pl. XXIV, Fig. 6
Pilocarpine with Platinum Chloride .....	Pl. V, Fig. 2
Platinum Chloride .....	Pls. IV, V
Potassium Acetate .....	Pl. XII
Potassium Chromate .....	Pl. XXI
Potassium Cyanide .....	Pl. XXI
Potassium Ferrocyanide .....	Pl. XX
Potassium Hydroxide .....	Pls. XV, XVI
Potassium Iodide .....	Pl. XVIII
Potassium Permanganate .....	Pl. XXIII
Quinine with Ammonium Thiocyanate .....	Pl. XXV, Figs. 4, 5
with Potassium Acetate .....	Pl. XII, Fig. 6
with Potassium Chromate .....	Pl. XXI, Fig. 6
with Sodium Phosphate .....	Pl. VII, Fig. 6
with Wagner's Reagent .....	Pl. XII, Fig. 2
Quinidine with Ammonium Thiocyanate .....	Pl. XXV, Fig. 3
with Gold Chloride .....	Pl. II, Fig. 6
with Mercuric Chloride .....	Pl. IX, Fig. 3
with Potassium Ferrocyanide .....	Pl. XX, Fig. 3
with Potassium Iodide .....	Pl. XVIII, Fig. 6
Quinoline with Chromic Acid .....	Pl. XXIII, Fig. 1
with Gold Chloride .....	Pl. III, Fig. 1
with Kraut's Reagent .....	Pl. XIII, Fig. 4
with Mercuric Chloride .....	Pl. IX, Fig. 4
with Millon's Reagent .....	Pl. XXVI, Fig. 4
with Picric Acid .....	Pl. XIX, Fig. 6
with Platinum Chloride .....	Pl. V, Fig. 3
with Potassium Ferrocyanide .....	Pl. XX, Fig. 4
with Wagner's Reagent .....	Pl. XII, Fig. 3
Saccharin .....	Pl. V
Scopolamine with Gold Chloride .....	Pl. III, Fig. 2
with Wagner's Reagent .....	Pl. XII, Fig. 4
Sodium Carbonate .....	Pls. XIII, XIV
Sodium Nitroprusside .....	Pl. IX
Sodium Phosphate .....	Pl. VII
Sparteine with Gold Chloride .....	Pl. III, Fig. 3
with Palladous Chloride .....	Pl. VII, Fig. 2
Strychnine with Ammonium Thiocyanate .....	Pl. XXV, Fig. 6
with Chromic Acid .....	Pl. XXIII, Fig. 2
with Gold Chloride .....	Pl. III, Fig. 4
with Marne's Reagent .....	Pl. XVII, Fig. 6
with Mayer's Reagent .....	Pl. XVI, Figs. 4, 5
with Palladous Chloride .....	Pl. VII, Fig. 3
with Platinum Chloride .....	Pl. V, Fig. 4
with Picric Acid .....	Pl. XX, Fig. 1

## 110 SOME MICROCHEMICAL TESTS FOR ALKALOIDS

Strychnine with Potassium Hydroxide.....	Pl. XVI, Fig. 1
with Mercuric Chloride .....	Pl. IX, Fig. 5
with Sodium Carbonate .....	Pl. XIV, Fig. 6
with Zinc-Chlor-Iodide .....	Pl. XXVII, Figs. 4, 5
Sulphuric Acid .....	Pl. XX
Thebaine with Potassium Hydroxide .....	Pl. XVI, Fig. 2
Tropacocaine with Chromic Acid .....	Pl. XXIII, Fig. 3
with Gold Chloride .....	Pl. III, Fig. 5
with Kraut's Reagent .....	Pl. XIII, Fig. 5
with Marme's Reagent .....	Pl. XVIII, Fig. 1
with Mayer's Reagent .....	Pl. XVI, Fig. 6
with Palladous Chloride .....	Pl. VII, Fig. 4
with Picric Acid .....	Pl. XX, Fig. 2
with Platinum Chloride .....	Pl. V, Fig. 5
with Potassium Permanganate .....	Pl. XXIII, Fig. 6
with Zinc-Chlor-Iodide .....	Pl. XXVII, Fig. 6
Wagner's Reagent .....	Pls. X, XI, XII
Yohimbine with Potassium Cyanide .....	Pl. XXI, Fig. 8
Zinc Chloride .....	Pls. XXVI, XXVII
Zinc-Chlor-Iodide .....	Pl. XXVII

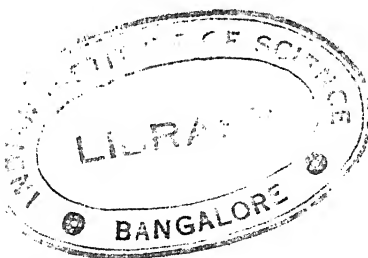


PLATE I.



FIG. 1.—Anhalonine 1 : 200.



FIG. 2.—Apomorphine 1 : 500.

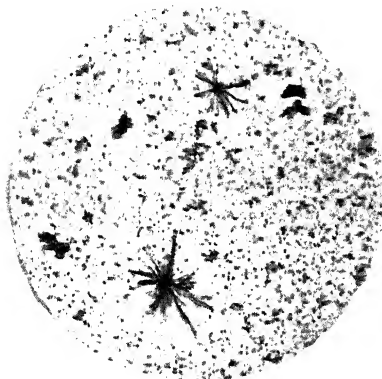


FIG. 3.—Benzoyl-ecgonine 1 : 50.

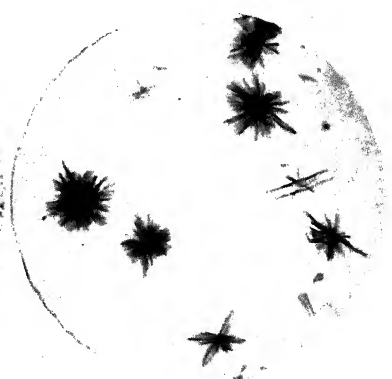


FIG. 4.—Caffeine 1 : 50.

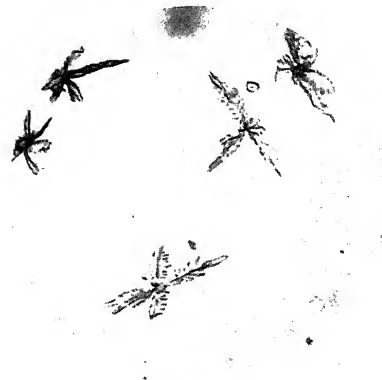


FIG. 5.—Cocaine 1 : 500.

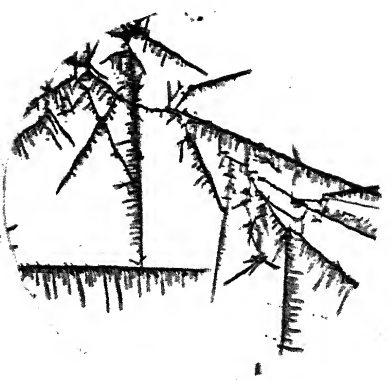


FIG. 6.—Cocaine 1 : 1000.

Crystals formed with gold chloride (X150).

PLATE II.



FIG. 1.—Cytisine 1 : 200.

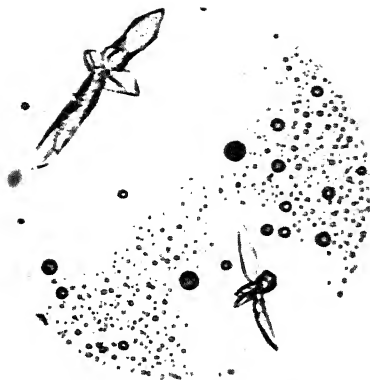


FIG. 2.—Homatropine 1 : 200.



FIG. 3.—Hyoscyamine 1 : 50.

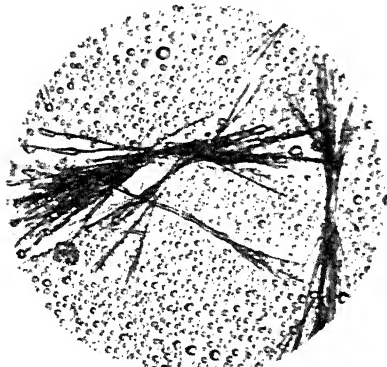


FIG. 4.—Narceine 1 : 50.



FIG. 5.—Nicotine 1 : 1000.



FIG. 6.—Quinidine 1 : 200.

Crystals formed with gold chloride ( $\times 150$ ).

PLATE III.



FIG. 1.—Quinoline 1 : 1000.



FIG. 2.—Scopolamine 1 : 10000.



FIG. 3.—Sparteine 1 : 200.



FIG. 4.—Strychnine 1 : 500.  
Crystals formed with gold chloride ( $\times 150$ ).



FIG. 5.—Tropacocaine 1 : 1000, with gold chloride ( $\times 150$ ).



FIG. 6.—Cocaine 1 : 50, with ferric chloride ( $\times 150$ ).

PLATE IV.



FIG. 1.—Anhalonine 1 : 200.

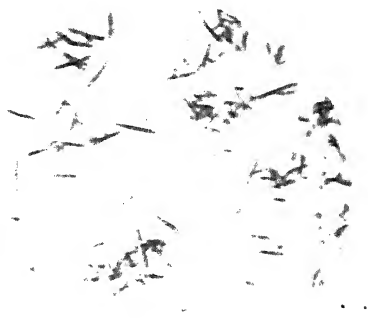


FIG. 2.—Brucine 1 : 50.



FIG. 3.—Calycanthine 1 : 1000.



FIG. 4.—Cinchonidine 1 : 1000.

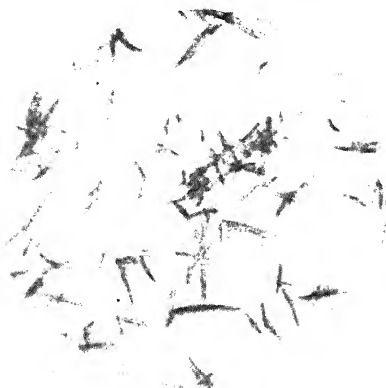


FIG. 5.—Cocaine 1 : 500.



FIG. 6.—Hydrastinine 1 : 500.  
Crystals formed with platinum chloride ( $\times 150$ ).



PLATE V.

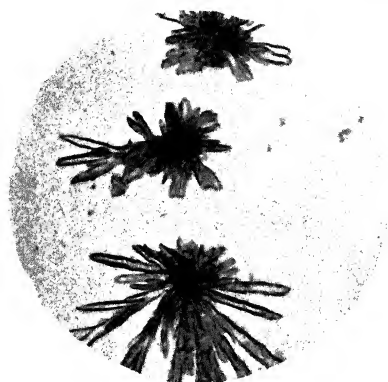


FIG. 1.—Narceine 1 : 50.

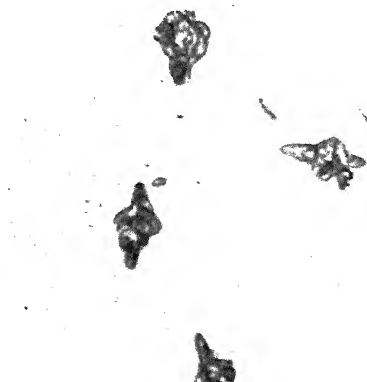


FIG. 2.—Pilocarpine 1 : 50.



FIG. 3.—Quinine 1 : 500.

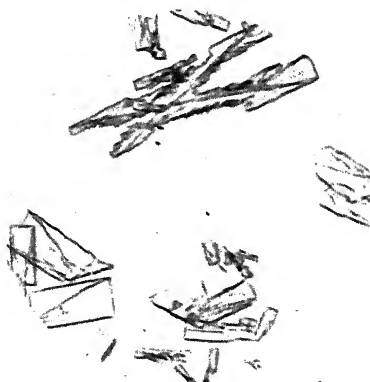


FIG. 4.—Strychnine 1 : 500.

Crystals formed with platinum chloride (X150).



FIG. 5.—Tropacocaine 1 : 500, with platinum chloride (X150).

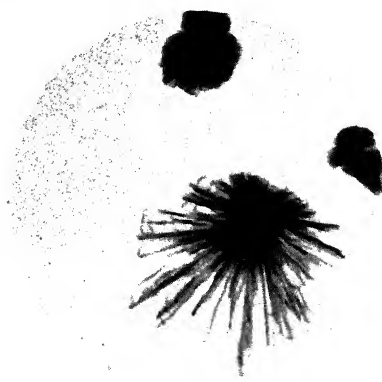


FIG. 6.—Brucine 1 : 50, with saccharine (X150).

PLATE VI.



FIG. 1.—Arecoline 1 : 50.

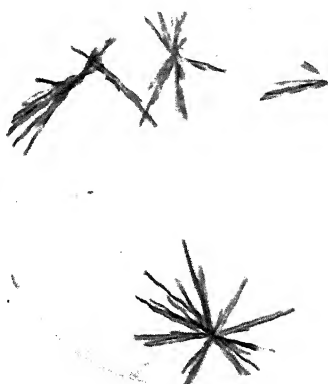


FIG. 2.—Brucine 1 : 500.



FIG. 3.—Cocaine 1 : 500.



FIG. 4.—Narceine 1 : 50.



FIG. 5.—Hydrastinine 1 : 500.

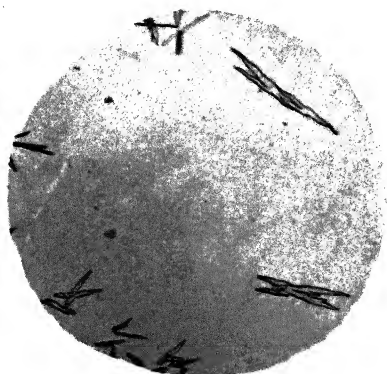


FIG. 6.—Calycanthine 1 : 1000.

Crystals formed with palladous chloride ( $\times 150$ ).

PLATE VII.

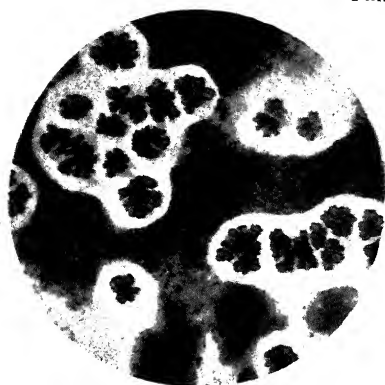


FIG. 1.—Papaverine 1 : 50.

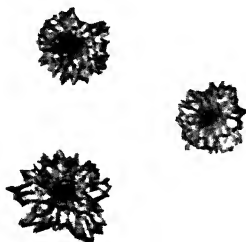


FIG. 2.—Sparteine 1 : 50.

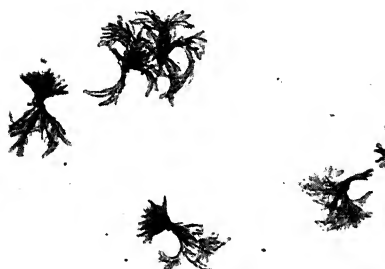


FIG. 3.—Strychnine 1 : 500.

Crystals formed with palladous chloride ( $\times 150$ ).



FIG. 4.—Tropacocaine 1 : 100.

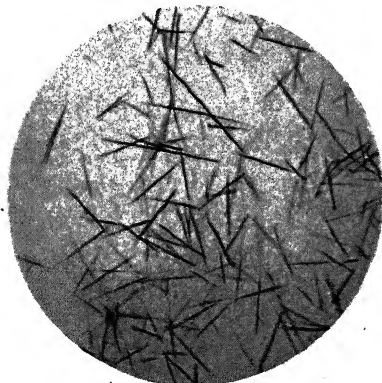


FIG. 5.—Cinchonidine 1 : 200.

Crystals formed with sodium phosphate 1 : 200.

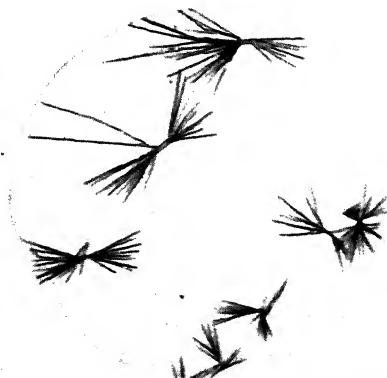


FIG. 6.—Quinine 1 : 200.

PLATE VIII.

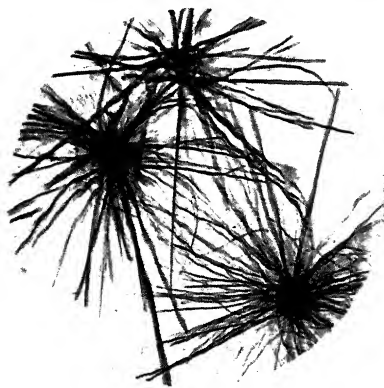


FIG. 1.—Caffeine 1 : 50.

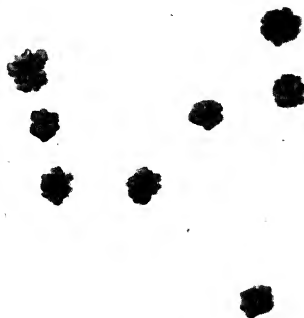


FIG. 2.—Corydaline 1 : 50.



FIG. 3.—Cytisine 1 : 50.



FIG. 4.—Dionine 1 : 50.



FIG. 5.—Heroin 1 : 200.



FIG. 6.—Morphine 1 : 50.

Crystals formed with mercuric chloride ( $\times 150$ ).

PLATE IX.



FIG. 1.—Nicotine 1 : 200.

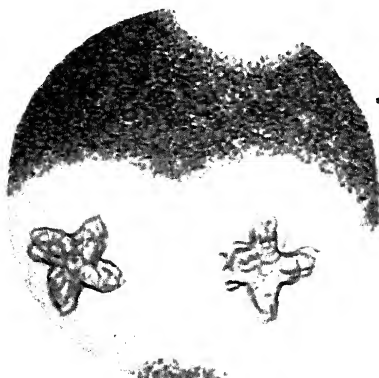


FIG. 2.—Papaverine 1 : 50.

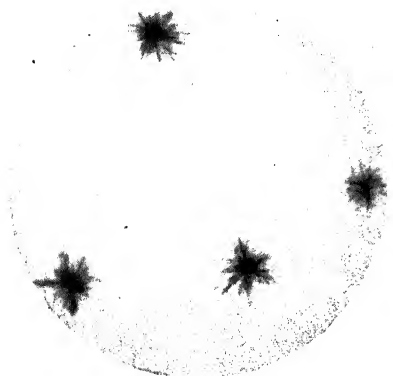


FIG. 3.—Quinidine 1 : 200.

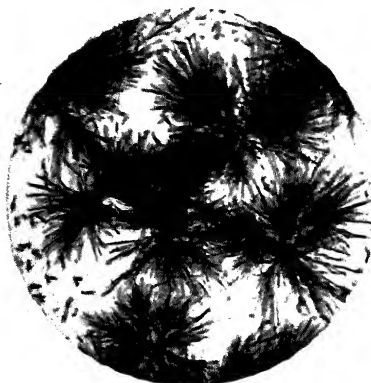


FIG. 4.—Quinoline 1 : 200.

Crystals formed with mercuric chloride (X150).



FIG. 5.—Strychnine 1 : 500, with mercuric chloride (X150).

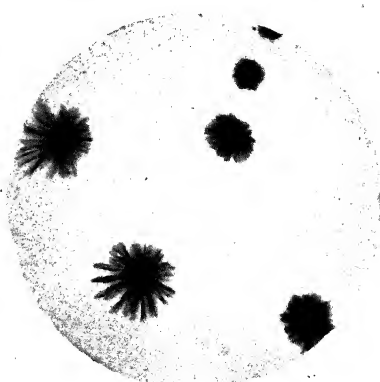


FIG. 6.—Brucine 1 : 50, with sodium nitroprusside.

PLATE X.



FIG. 1.—Aspidospermine 1 : 50.

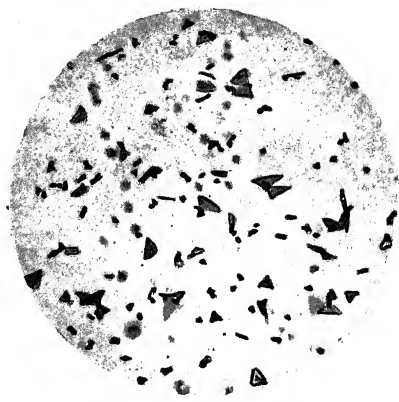


FIG. 2.—Atropine 1 : 500.



FIG. 3.—Atropine 1 : 500 ( $\times 300$ ).

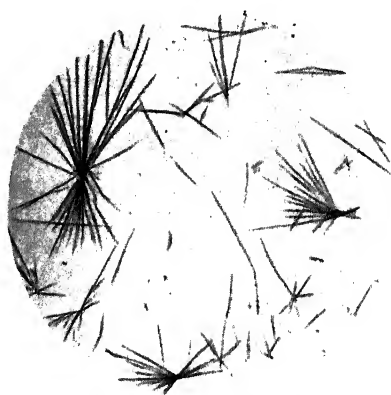


FIG. 4.—Berberine 1 : 500.



FIG. 5.—Brucine 1 : 500.



FIG. 6.—Codeine 1 : 50.

Crystals formed with Wagner's reagent ( $\times 150$ ).

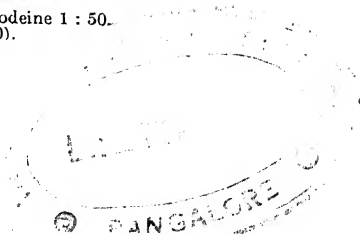


PLATE XI

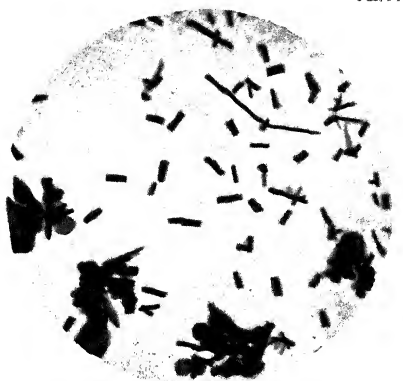


FIG. 1.—Cytisine 1 : 200.



FIG. 2.—Deltaine 1 : 50.

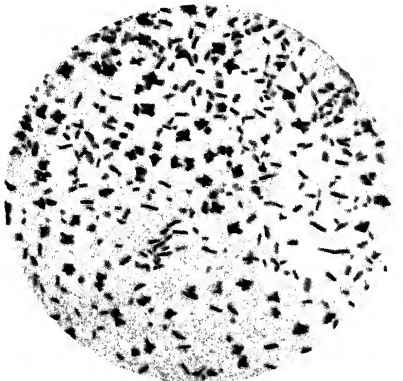


FIG. 3.—Homatropine 1 : 500.



FIG. 4.—Homatropine 1 : 200.

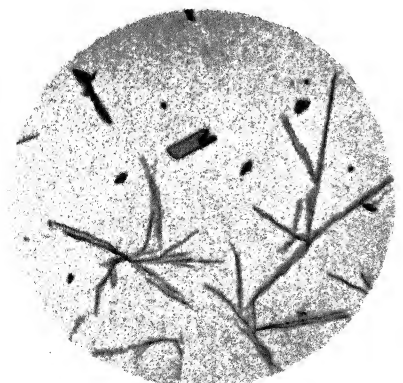


FIG. 5.—Hyoscyamine 1 : 50.



FIG. 6.—Morphine 1 : 200.

Crystals formed with Wagner's reagent ( $\times 150$ ).

PLATE XII.

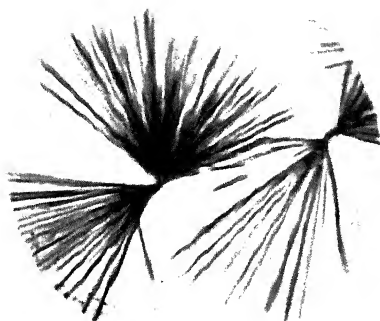


FIG. 1.—Narceine 1 : 500.



FIG. 2.—Quinine 1 : 50.

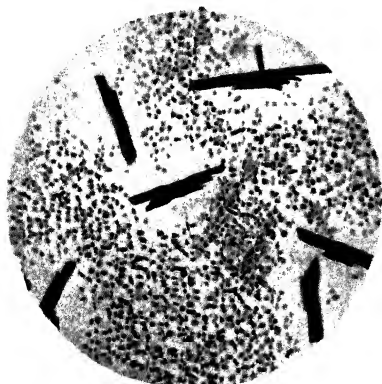


FIG. 3.—Quinoline 1 : 200.

Crystals formed with Wagner's reagent ( $\times 150$ ).



FIG. 4.—Scopolamine 1 : 50.



FIG. 5.—Narcotine 1 : 200.

Crystals formed with potassium acetate ( $\times 150$ ).

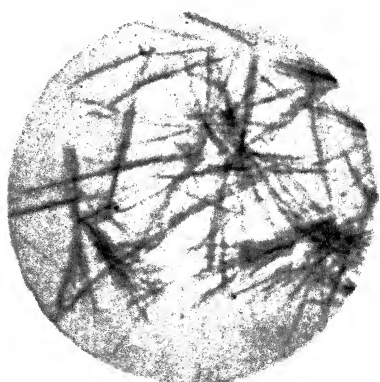


FIG. 6.—Quinine 1 : 35.



PLATE XIII.



FIG. 1.—Arecoline 1 : 500.



FIG. 2.—Camphor 1 : 50.

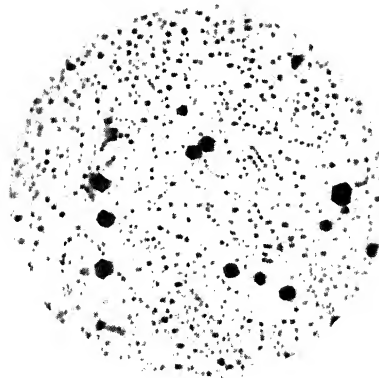


FIG. 3.—Ecgonine 1 : 200.

Crystals formed with Kraut's reagent (X150).

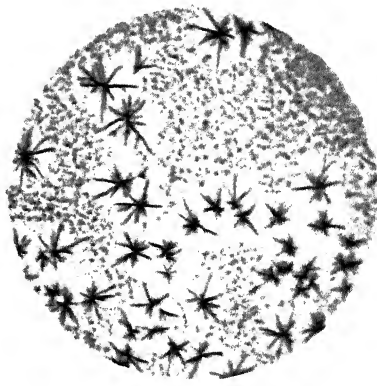


FIG. 4.—Quinine 1 : 1000.



FIG. 5.—Tropacocaine 1 : 1000, with Kraut's reagent (X150).

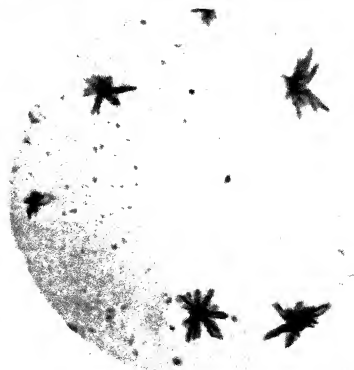


FIG. 6.—Aconitine 1 : 500, with sodium carbonate.

PLATE XIV

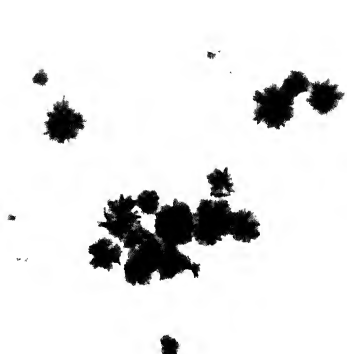


FIG. 1.—Cinchonine 1 : 500.

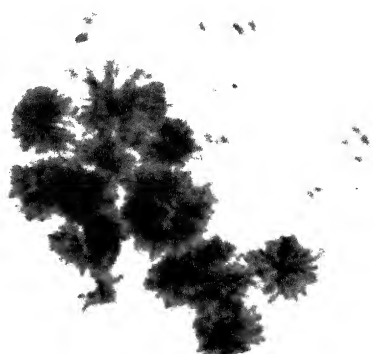


FIG. 2.—Cocaine 1 : 500.

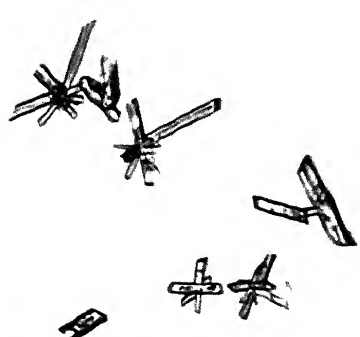


FIG. 3.—Dionine 1 : 50.



FIG. 4.—Morphine 1 : 50.



FIG. 5.—Narcotine 1 : 1000.

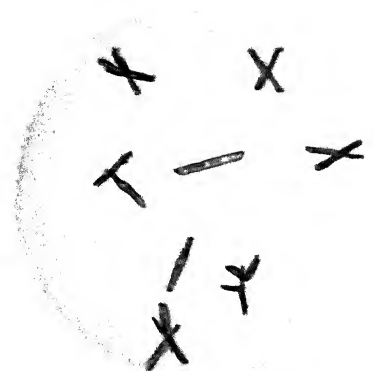


FIG. 6.—Strychnine 1 : 500.

Crystals formed with sodium carbonate ( $\times 150$ ).

PLATE XV



FIG. 1.—Aspidospermum 1 : 1000.

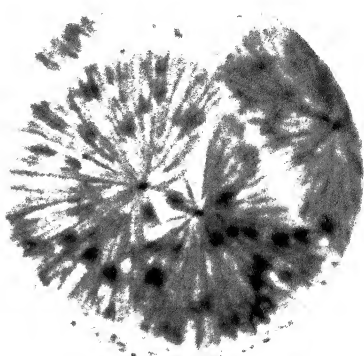


FIG. 2.—Bismuthum 1 : 500 X 77.

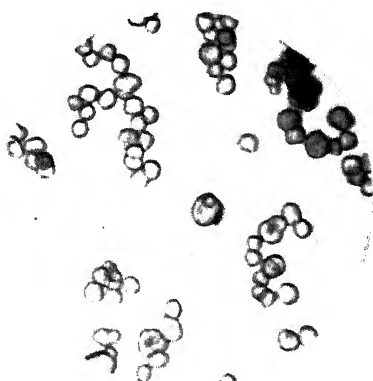


FIG. 3.—Cinchonidine 1 : 200.

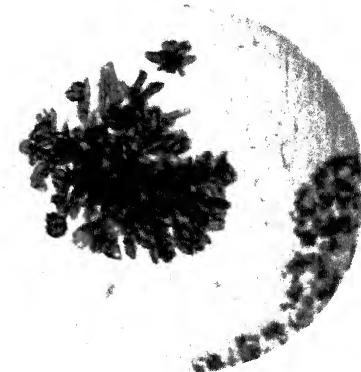


FIG. 4.—Hydrastine 1 : 50.

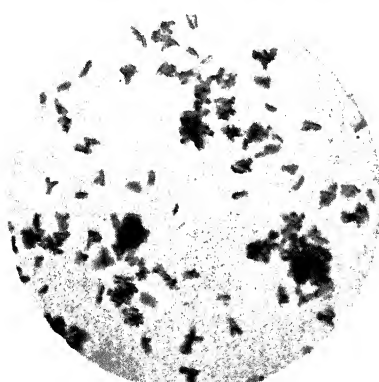


FIG. 5.—Papaverine 1 : 200.  
Crystals formed with potassium hydroxide (X 150).



FIG. 6.—Narceine 1 : 50.

PLATE XXI

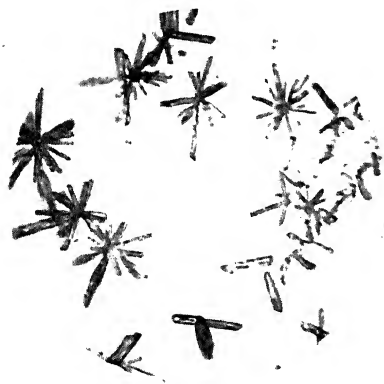


FIG. 1.—Strychnine 1 : 500.

Crystals formed with potassium hydrate. (x150).



FIG. 2.—Strychnine 1 : 500.



FIG. 3.—Morphine 1 : 200 (x300).

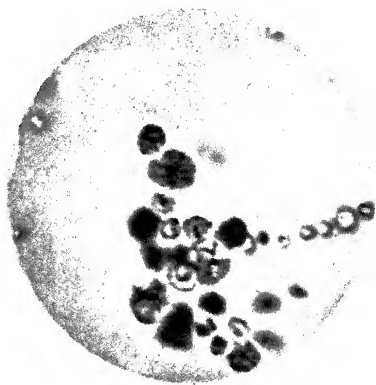


FIG. 4.—Strychnine 1 : 500.

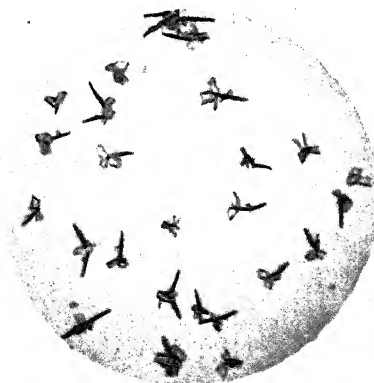


FIG. 5.—Strychnine 1 : 500.

Crystals formed with Mayer's reagent. (x150).



FIG. 6.—Tropaeoline 1 : 10000.

PLATE XVII.

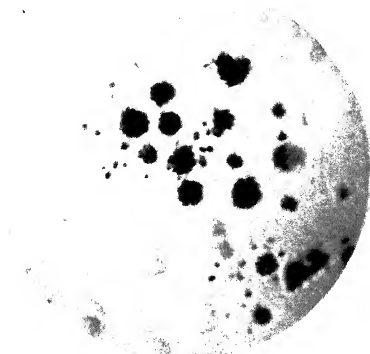


FIG. 1.—Codeine 1 : 200.



FIG. 2.—Codeine 1 : 200.



FIG. 3.—Codeine 1 : 200.



FIG. 4.—Codeine 1 : 200.

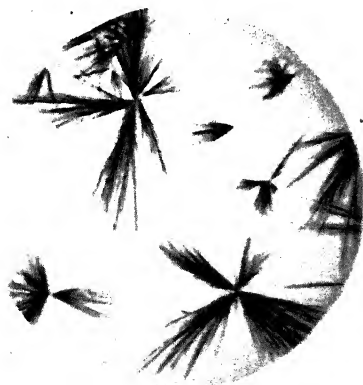


FIG. 5.—Morphine 1 : 200.  
Crystals formed with Marme's reagent ( $\times 150$ )

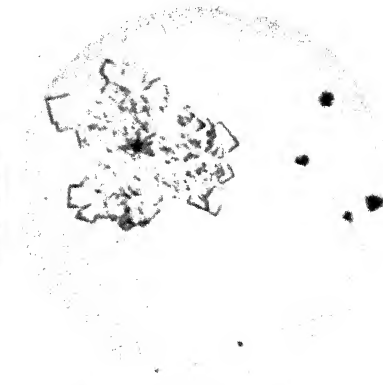


FIG. 6.—Strychnine 1 : 500.

PLATE XVII.

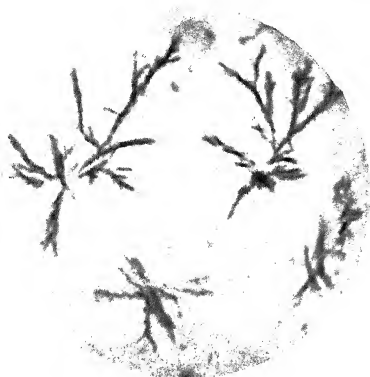


FIG. 1.—Tropacocaine 1 : 1000, with Marmer's reagent ( $\times 150$ ).

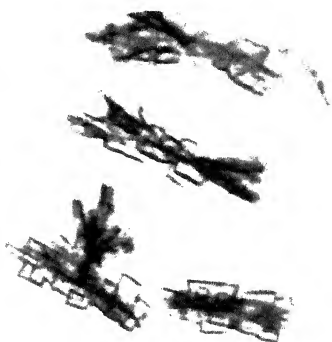


FIG. 2.—Tropacocaine 1 : 1000.

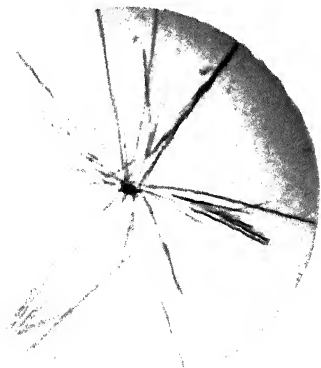


FIG. 3.—Codeine 1 : 50.

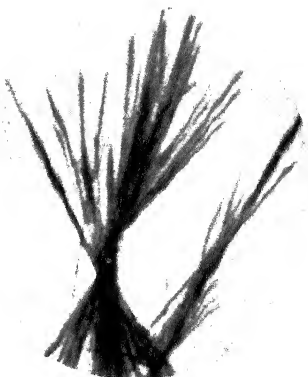


FIG. 4.—Morphine 1 : 50.

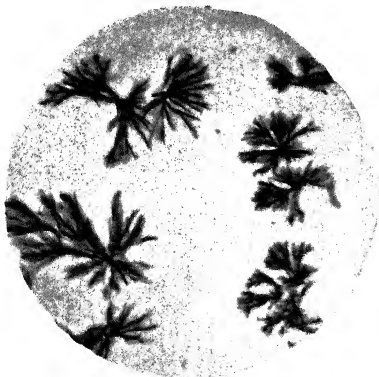


FIG. 5.—Peronine 1 : 200.

Crystals formed with potassium iodide :  $\times 150$ .



FIG. 6.—Quinidine 1 : 200.

PLATE XIX.



FIG. 1.—Atropine 1 : 50.

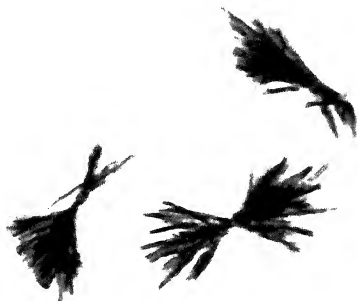


FIG. 2.—Quinine 1 : 500.

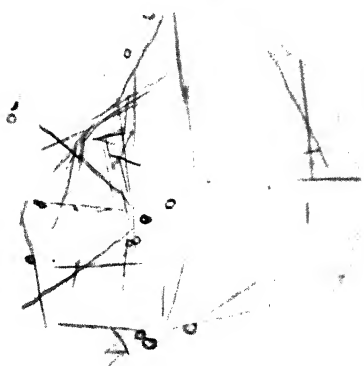


FIG. 3.—Cytisine 1 : 50.



FIG. 4.—Heroin 1 : 200.



FIG. 5.—Hydrastinine 1 : 200.

FIG. 6.—Quinine 1 : 1000.  
Crystals formed with picric acid (X150).

PLATE XX



FIG. 1.—Strychnine 1 : 500.

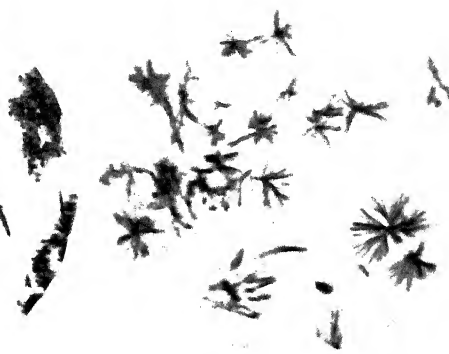


FIG. 2.—Ergonine (1 : 500).  
Crystals formed with picric acid ( $\times 150$ ).

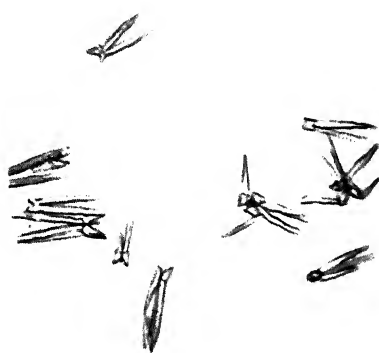


FIG. 3.—Quinidine 1 : 50.



FIG. 4.—Quinine 1 : 200.  
Crystals formed with potassium ferrioxalate ( $\times 150$ ).



FIG. 5.—Berberine 1 : 500, with hydrochloric acid ( $\times 150$ ).



FIG. 6.—Berberine 1 : 500, with sulphuric acid ( $\times 150$ ).



PLATE XXI



FIG. 1.—Bruene 1 : 50.

Crystals formed with potassium cyanide (X150).



FIG. 2.—Fibroine 1 : 200.



FIG. 3.—Yohimbine 1 : 200, with potassium cyanide (X150).

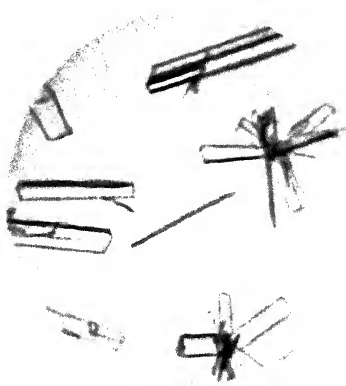


FIG. 4.—Codeine 1 : 50, with potassium chromate.



FIG. 5.—Morphine 1 : 50.

Crystals formed with potassium chromate (X150).

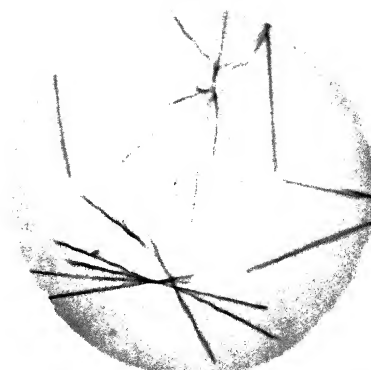


FIG. 6.—Quinine 1 : 200.

LIBRARY

PLATE XXII.



FIG. 1.—Brucine 1 : 500.



FIG. 2.—Calycanthine 1 : 50.

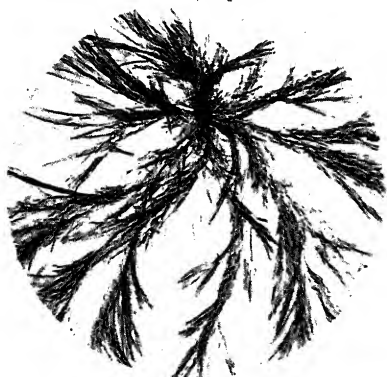


FIG. 3.—Cocaine 1 : 200.



FIG. 4.—Codeine 1 : 50.



FIG. 5.—Hydrastinine 1 : 200.

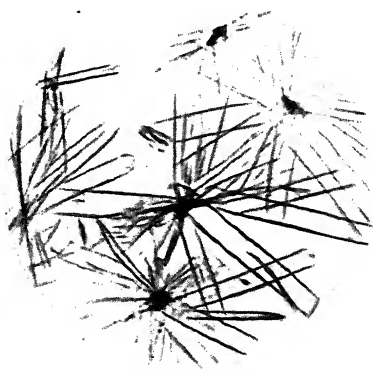


FIG. 6.—Hydrastinine 1 : 200.

Crystals formed with chromic acid ( $\times 150$ ).



PLATE XXIII.



FIG. 1.—Quinoline 1 : 50.  
Crystals formed with chromic acid (X150).



FIG. 2.—Strychnine 1 : 500.



FIG. 3.—Tropacocaine 1 : 100, with chromic acid (X150).



FIG. 4.—Cocaine 1 : 200, with potassium permanganate.



FIG. 5.—Hydrastinine 1 : 500.  
Crystals formed with potassium permanganate (X150).



FIG. 6.—Tropacocaine 1 : 1000.

LIBRARY

PLATE XXIV.

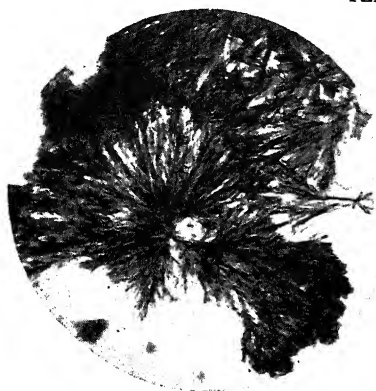


FIG. 1.—Betaine 1 : 200.

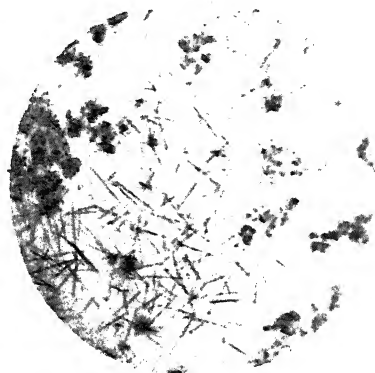


FIG. 2.—Choline 1 : 200.

Crystals formed with phosphomolybdic acid ( $\times 150$ ).

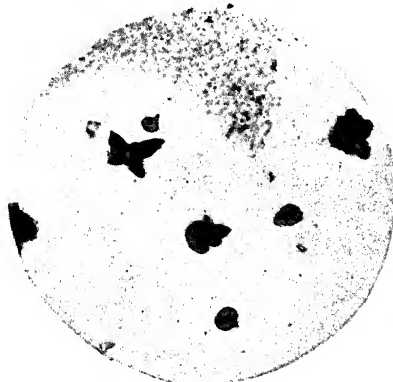


FIG. 3.—Anhalonine 1 : 200.

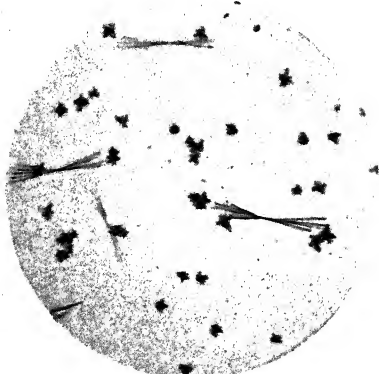


FIG. 4.—Betaine 1 : 1000.

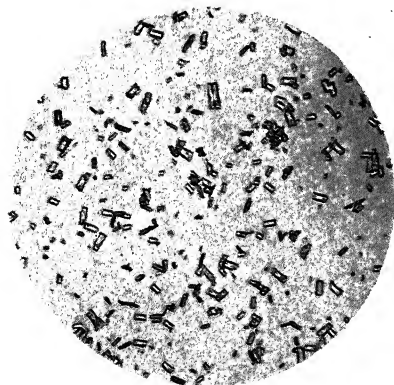


FIG. 5.—Coniine 1 : 200.

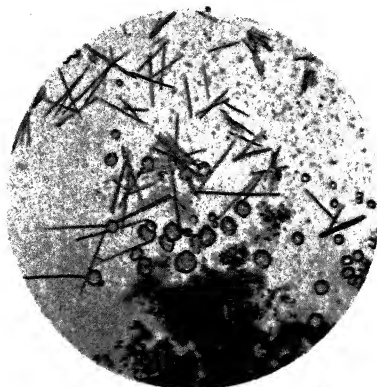


FIG. 6.—Pilocarpidine 1 : 50.

Crystals formed with phosphotungstic acid ( $\times 150$ ).

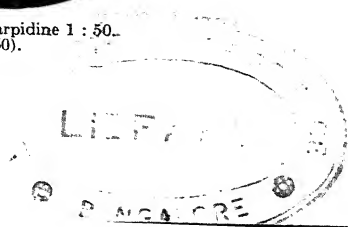


PLATE XXV.

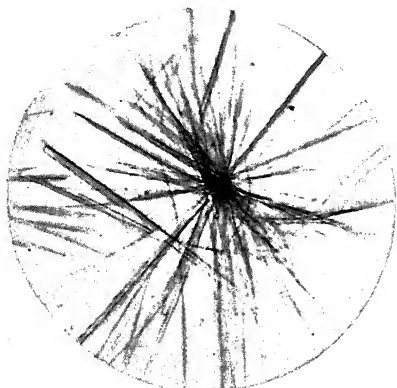


FIG. 1.—Brucine 1 : 50.

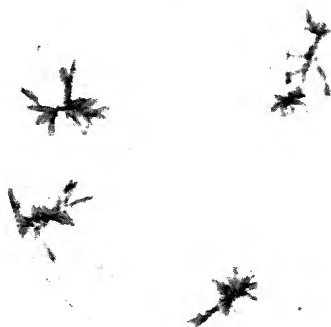


FIG. 2.—Codeine 1 : 50.

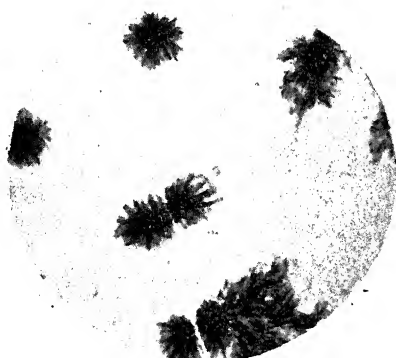


FIG. 3.—Quinidine 1 : 200.



FIG. 4.—Quinine 1 : 35.



FIG. 5.—Quinine 1 : 35.

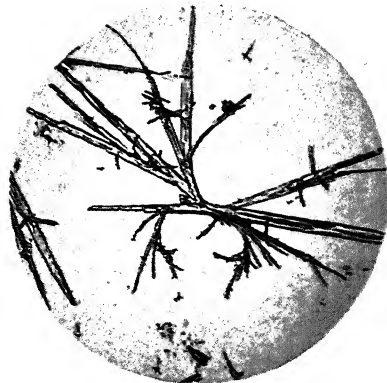


FIG. 6.—Strychnine 1 : 500.  
Crystals formed with ammonium thiocyanate (X150).

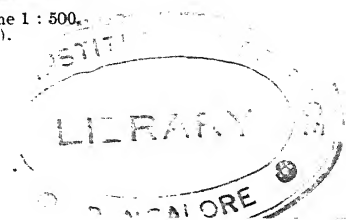


PLATE XXVI.

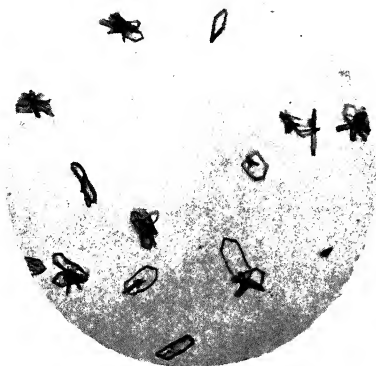


FIG. 1.—Brucine 1 : 1000.

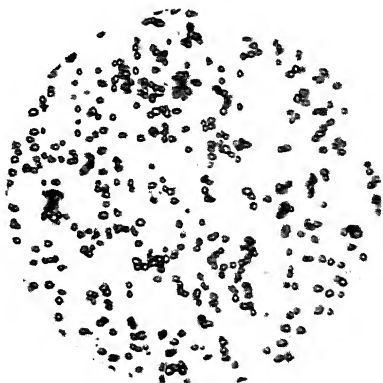


FIG. 2.—Codeine 1 : 50.



FIG. 3.—Homatropine 1 : 50.

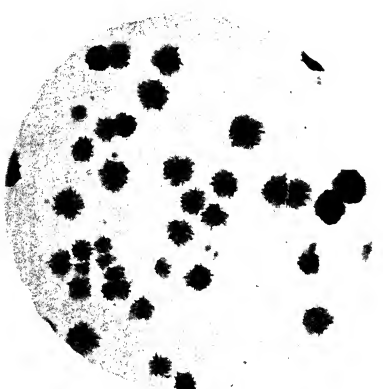


FIG. 4.—Quinoline 1 : 50.

Crystals formed with Millon's reagent ( $\times 150$ ).



FIG. 5.—Brucine 1 : 50.

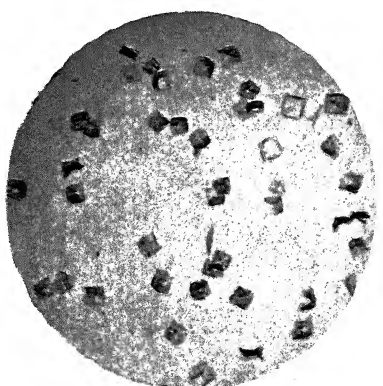


FIG. 6.—Papaverine 1 : 500.

Crystals formed with zinc chloride ( $\times 150$ ).

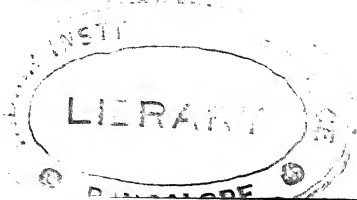


PLATE XXVII.

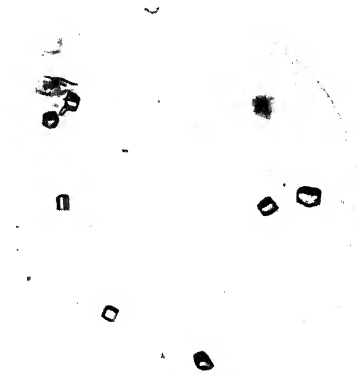


FIG. 1.—Chelidonine 1 : 500, with zinc chloride ( $\times 150$ ).



FIG. 2.—Codeine 1 : 50.



FIG. 3.—Codeine 1 : 50.

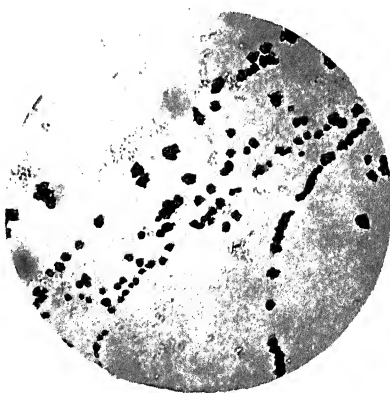


FIG. 4.—Strychnine 1 : 500.

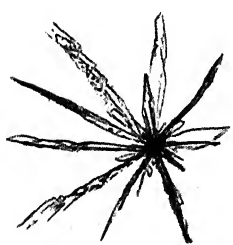


FIG. 5.—Strychnine 1 : 50.  
Crystals formed with zinc-chlor-iodide ( $\times 150$ ).



FIG. 6.—Tropacocaine 1 : 500.

